Studies On Transition Metal Complexes Of Nitrogen And Sulphur Containing Organic Molecules

ABSTRACT

A THESIS SUBMITTED TO THE ALIGARH MUSLIM UNIVERSITY, ALIGARH FOR THE DEGREE

OF

DOCTOR OF PHILOSOPHY IN CHEMISTRY

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH, INDIA.

MOHD. AHMAD ALI SHAH
M. Sc. M. Phil (Alig)

JUNE 1983

A B S T R A C T

Addition as well as substitution compounds of a few transition metal ions with sulphur and nitrogen containing bases have been studied under this project. The compounds have been characterised by elemental analyses, conductivity, infrared- and electronic spectral and magnetic measurement studies. The soluble complexes formed only in solution have been studied potentiometrically following the Irving-Rossotti's techniques. Their stability constants, enthalpy and entropy have been evaluated.

There are two known methods for the synthesis of metal dithiocarbamates namely (i) by direct insertion method and (ii) by the action of sodium or ammonium salt of the dithiocarbamate on metal ions. The solid complexes of ammonium tetramethylenedithiocarbamate and β-naphthylamine-dithiocarbamate with Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Cd(II) were synthesized in order to examine whether the dithiocarbamato moiety acts as a monodentate or a bidentate ligand. Their dual nature was distinguished from their IR spectra on the basis of the C=S stretching frequency. It has been found that the dithiocarbamates were symmetrically coordinated to all the metal ions.

The tetramethylenedithiocarbamate complexes of Mn(II) and Co(II) have been found to be tetrahedral whereas those of Ni(II) and Cu(II) are square planar. The magnetic measurement of Fe(III) complex showed the spin equilibrium states in octahedral environment. The β-naphthylamine-dithiocarbamate has also been shown to be symmetrically coordinated. The Fe(III) complex of this ligand was different from that of the tetramethylenedithiocarbamate in the sense that only two of the three chlorine atoms were replaced by the dithiocarbamate group. Fe(III) is nevertheless octahedral through chlorine bridging. The Co(II), Ni(II), and Cu(II) complexes have been found to be square planar and that of Mn(II) has been proposed to be tetrahedral.

The dihydrobis-, hydrotris- and tetrakis(2-mercaptobenzo-thiazolyl)borates have been synthesized by refluxing 2-mercap-tobenzothiazole with potassium borohydride in dimethyl-formamide in appropriate amounts. The formation of the Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) borates were ascertained by the evolution of hydrogen gas corresponding to the ratio of the reactants used. They were further characterized by -BH and B-H peaks and their elemental analyses. The coordination of the metal ions with the nitrogen heteroatom has also been ascertained by the presence of M-N peaks in 400-380 cm^{-1} region.

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Metal complexes of tetrakis(2-mercaptobenzothiazolyl)borate were characterized by the absence of -BH peak in their infrared spectra. The Mn(II) complex is found to be octahedral, coordinating only through three nitrogen atoms of a tetrakis borate anion which is in conformity with the geometry of boron. The Co(II) and Ni(II) complexes are tetrahedral and square planar respectively showing coordination through only two nitrogen atoms. No conclusive result could be obtained in the case of Cu(II) complex and, therefore, its structure could not be proposed.

The solution study of the complex formation of the lanthanide(III) ions with 2-amino-5-mercapto-1,3,4-thiadiazole have been done with a view to study the order of the stability

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Certified that the work embodied in this thesis entitled "Studies on the Transition Metal Complexes of Nitrogen and Sulphur Containing Organic Molecules" is the original research work carried out by Mr. Mohd. Ahmad Ali Shah under my supervision. This work is suitable for the submission of the award of Ph.D. Degree of Aligarh Muslim University, Aligarh.

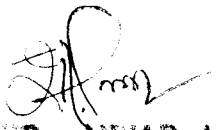
(K.S. SIDDIQI)

A C K N O W L E D G E M E N T

I take the opportunity to express my deep sense of gratitute towards Dr. K.S. Siddiqi, M.Sc., Ph.D.(Alig) for his guidance and suggestions in the interpretation of results. I am also very grateful to my respected teacher, Prof. S.A.A. Zaidi, M.Sc.(Alig), M.A. Ph.D.(Toronto), AMIC (London) for inspiring me during the course of this work.

I am indebted towards Prof. M. Rahman, Chairman, Department of Chemistry, A.M.U., Aligarh for providing research facilities. I am also thankful to all my research collegues for the help they have rendered to me from time to time.

Thanks are due to U.G.C. for the award of Teacher Fellowship and to the Government of Manipur for granting leave. Principal, Thoubal College, Thoubal Manipur is also acknowledged.



(MOHD. AHMAD ALI SHAH)

C O N T E N T S

LIST OF PUBLICATIONS

1. Behaviour of Tetramethylenedithiocarbamate and its Transition Metal Complexes.
   K.S. Siddiqi, M.A.A. Shah and S.A.A. Zaidi; Bull. Soc. Chim.(France) No. 1-2, I-49 (1983).

2. Complexes of Mn(II), Co(II) and Cu(II) metal ions with β-Naphthylamine Dithiocarbamate.
   K.S. Siddiqi, M.A.A. Shah and S.A.A. Zaidi; Indian J. Chemistry (In Press).

3. Stability constant of Nd(III), Sm(III), Gd(III), Tb(III), Dy(III) and Ho(III) complexes with 2-Amino-5-Mercapto-1,3,4-Thiadiazole.
   K.S. Siddiqi, M.A.A. Shah and S.A. A. Zaidi; Indian J. Chemistry (In Press).

4. Synthesis and Characterisation of poly(2-mercapto-benzothiazolyl)borate complexes of some transition metal ions.
   K.S. Siddiqi, M.A.A. Shah, M. Jaria and S.A.A. Zaidi; Acta. Chimica, Academiae Scientiarum Hungaricae (Communicated).

LIST OF TABLES

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A B S T R A C T

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CHAPTER I

INTRODUCTION

I N T R O D U C T I O N

Coordination compounds of transition metal ions have assumed importance in the recent years owing to their applications in medicine, agriculture and industry. Some aspects of transition metal complexes of nitrogen and sulphur containing organic molecules having biological, industrial and chemical significance are discussed below:

It is well known that cancer is caused due to the reproduction of malignant cells having a kinetic advantage over the body's defence mechanism. Therefore, a metal complex to be effective has to be sufficiently labile to outpace the cancerous growth[1]. From recent study of the antitumour activity of some neutral complexes of the type MA_2X_2 (A = amine, X = halogen) it has been suggested that the kinetic factors are of importance in determining the effective doses of the metal complexes[2]. The palladium and platinum complexes of 6-mercaptopurine (Fig. I) are also known to destroy adenocarcinomas[3]. In connection with the studies on the reaction of carcinogenic and anticancer compounds, the metal chelates of folic acid[4], riboflavine[5], adenine[6] and thioguanine[7] have been reported. Isoquinoline-1-carboxaldehyde thiosemicarbazole (Fig. II) has a broad range of carsinostatic activity and low toxicity[8]. In the pyrimidine group, 2-thiouracil has been found

to produce transient improvement in chronic granulocytic leukemia[9]. Ascorbic acid in conjuction with copper (II) ions is supposed to be toxic to malignant melanoma cells[10] and it has been tentatively reported to inhibit the growth of tumour in mice.

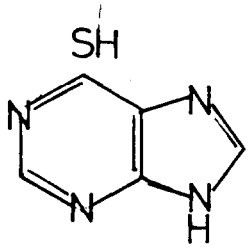


Fig. I

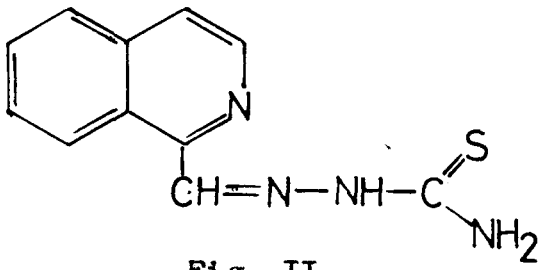


Fig. II

Thiazoles and 2-methylbenzothiazole complexes are being studied[11] because of their importance in biological systems. Certain metal complexes of thiazoles and imidazolethiol have been used as antioxidants and heat resistant materials[12,13] in addition to acting as fungicides and insecticides. Bismuthiol-I complex of tributyltin chloride has been used as corrosion inhibitor and in painting ships to prevent damage from marine organisms[14]. The pharmacological properties of 2-thiobarbituric acid have been reported[15,16] to have a rapid onset of action and rapid destruction in the body than their oxygen analogues. The 2-thiobarbiturate are providing very successful an intravenous anaesthetics. Thiocarbohydrazides are useful in many important anticarcinogenic and antibacterial properties[17]. The sulphathiazoles (Fig. III) and

sulphanilamido compounds also possess antibacterial activity[18]. The sulphanimides have much less antistreptococcal activity than 4,4'-diaminodiphenylsulphone[19].

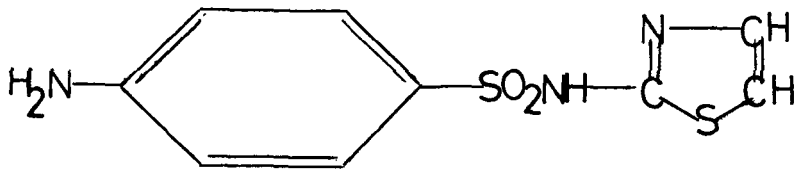


Fig. III

The dialkyldithiocarbamates are used as collectors of sulphides from finely milled ores[20]. The zinc (II) dialkyldithiocarbamate is used as vulcanisation accelerators[21,22] and $Au(S_2CNR_2)_3$ as pathways in photochemical[23,24] processes. The dithiocarbamates are also used in solar energy conversions[25,26]. Aqueous dispersions of dialkyldithiocarbamates resist rottings, fungal attack and pigment bleeding[27]. The nylon-66 textiles finished with sodium diethyldithiocarbamate and sodium 2-mercaptobenzothiazole salt or zinc diethyldithiocarbamate and zinc 2- mercaptobenzothiazole salts are found stable towards heat and light[28]. The dyeability of fibres is improved by incorporating $Ni(Et_2NCS_2)_2$ or $Zn(Et_2NCS_2)_2$ into the polymer. The dyed fibres have good light fastness, sublimation and drycleaning resistance[29].

The dithiocarbamates have been used in the identification and colorimetric determination of uranium[30,31]. Quantitative precipitation of UO_2^{+2} with dithiocarbamates under acidic conditions has also been reported[32,33]. Dibenzyldithiocarbamates are used as spectrophotometric reagent[34] and as coprecipitant for traces of heavy metals[35].

The complexes $[FeL_4]Cl$ (L = bipy, or phen) catalyse the conversion of water to oxygen[36]. Fe(III) 4,4',4'',4''' -tetracarboxyphthalocyanine can also be used as catalyst and is much more efficient than the hemin or other metal phthalocyanines[17]. Pyridoxal is important in enzymatic transamination and the reaction is catalysed by iron(III). Metal tetrahydroborates have also been used as catalysts[38,39] and as a reagent in metal hydride syntheses[40,41].

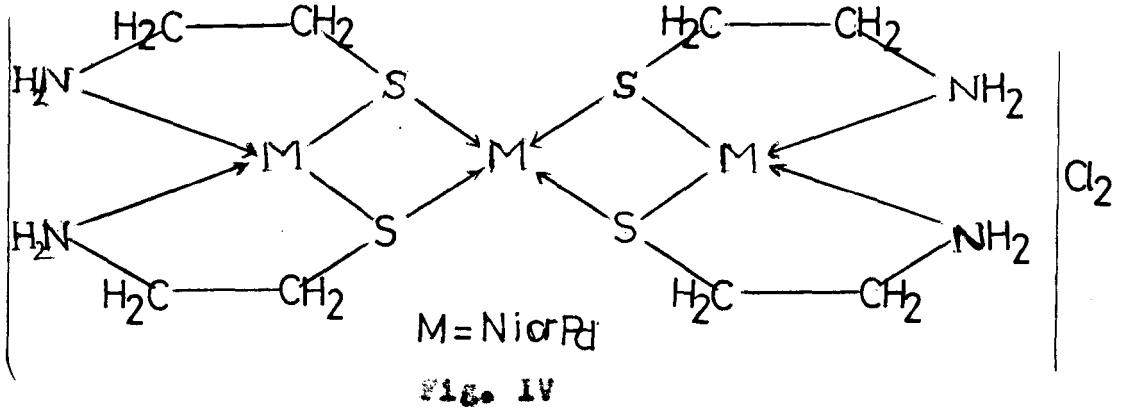


Fig. IV

The i.r. spectral studies of the transition metal complexes with thiazoles and imidazoletniol have established the bonding of the ligand through the nitrogen atom[42-44]. In a few cases, thiazoles

have also been shown to act as a bridging ligand[45]. The nitrogen and sulphur substituted thiosemicarbazole complexes of Cu(I) have been found to be polymeric, the metal ion being bound through both the nitrogen and sulphur of the thiosemicarbazole moiety[46]. 2-Aminoethanethiol yields two types of complexes with transition metal ions[47] viz. (i) the monomeric bis-ligand complexes $M(H_2NCH_2-CH_2S)_2$ (M=Ni, Pd) and (ii) the trinuclear cationic complex (Fig. IV). The structure of its nickel complex has been confirmed by X-ray diffraction method[48]. The reaction of zinc-ethanoate with 1,4,8,11-tetrathioundecane gives trimetallic complex (Fig. V) which transmetallates on treatment with $[Ni(H_2O)_6]^{+2}$ to give the corresponding trinickel(II) complex[49].

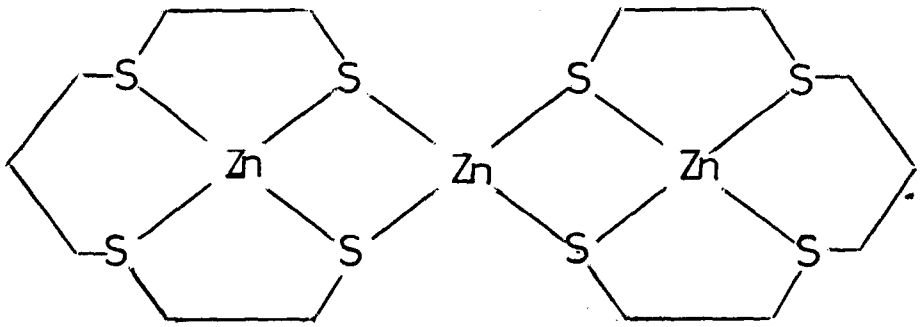


Fig. V

A few complexes of zinc with benzothiazole[50] and 2,4-dimercapto-S-triazole [4,3-b]-1,3,4-thiadiazole[51] (Fig. VI) have

been reported where the first complex has been shown to be five coordinated. The crystal structure of [NBu_4]-[$Zn(O_2CNMe_2)_2$ 2 ($u = O_2CNe$)] contains a square pyramidal ZnO_4O unit[52]. The compound [$Cd(NL)_2X_2$] (X = Cl, Br, I and L = 4,6-dimethyl-2(1H)

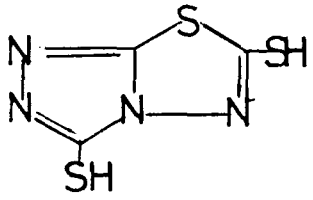


Fig. VI

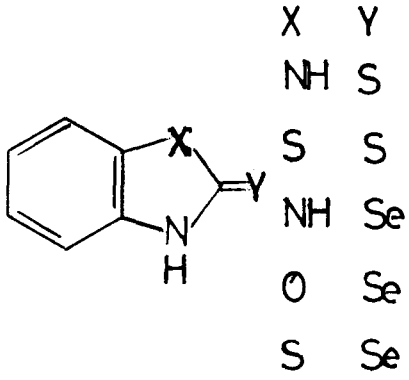


Fig. VII

pyrimidinethione) has been reported to have a polymeric halogen bridged structure which differs from the tetrahedral monomeric[53,54] Zn(II) and Hg(II) complexes. Cadmium complexes with the mercapto and the selenide ligands (Fig. VII) have also been reported[55]. Out of the cadmium(II) complexes with a number of dimercaptodicarboxylic acids and thioethers, the complex [$CdLCl_2$](where L = Fig. VIII) has also been shown to involve a square planar geometry at the metal[56]. The complexes [$Cd(NL)_2$], [$CdL(H_2O)_2$] (NL = Fig. VI) have been described to have a tetrahedral geometry[51].

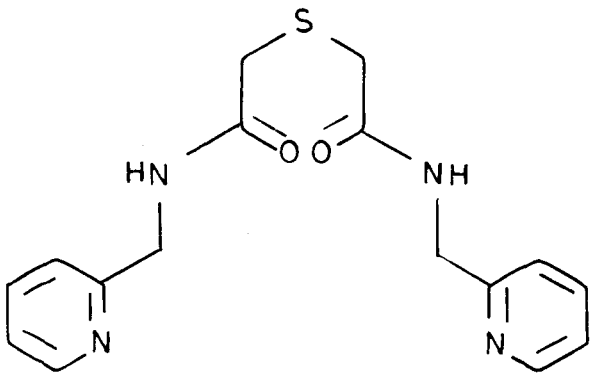


Fig. VIII

A number of stable uranyl(VI)dithiocarbamates have been characterized and reported as crystalline species containing ethanol of crystallisation[57]. Yellow or [illegible] crystals of $UO_2(DTC)_2(Me_3NO)$ has been obtained by treating $UO_2(NO_3)_2.6H_2O$ with a stoichiometric amount of potassium diethyldithiocarbamate and a slight excess of trimethylamine N-oxide (Me_3NO) in methanol[58]. The basic structure of the above complex corresponds to $UO_2(DTC)_2(Ph_3PO)$ and $UO_2(DTC)_2(Ph_3AsO)$ having uranium atom in the seven coordinate pentagonal bipyramidal environment (Fig. IX). X-ray powder patterns for quadrivalent thorium, uranium, neptunium and plutonium diethyldithiocarbamates have been shown to have similar structures[59].

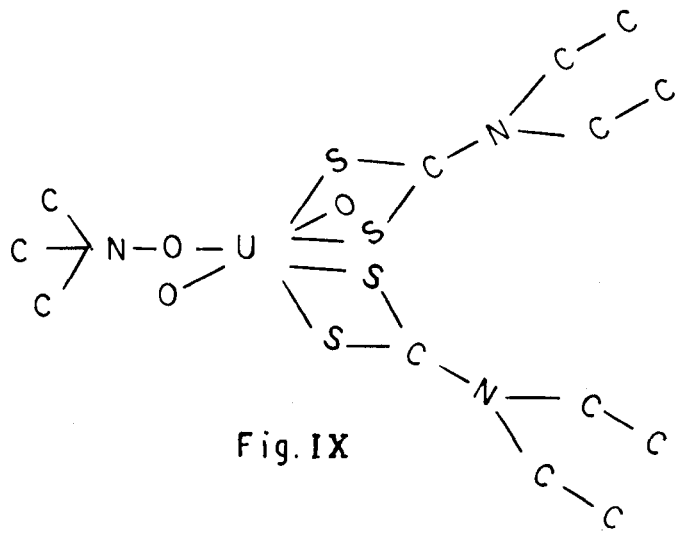
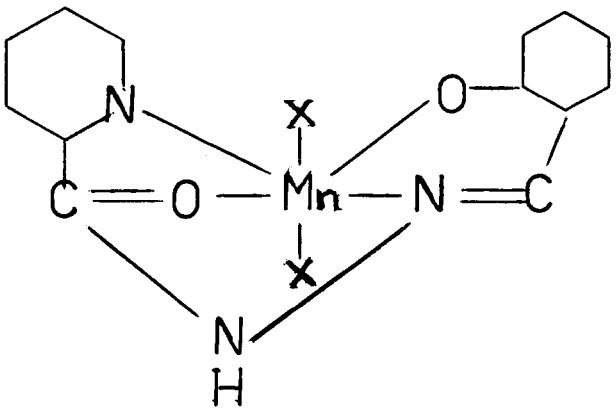


Fig. IX

Electrochemical studies on $[Fe(S_2CNR_2)_3]$ (NR_2=pyrolidine) have shown that both one electron oxidation and one electron reduction can occur in most solvents[60]. On the basis of structural study the compound $[FeI_2\{S_2C(py)\}_2]$ should be formulated as $[FeI\{S_2C(py)\}_2]0.5I_2$, containing a distorted pyramidal coordinated sphere with the iodine atom in the apical position[61]. A similar structure has been demonstrated for $[Fe(NCS)(S_2CNEt_2)_2]$[62].

X-ray crystal structure of $K[Mn(EDTA)].2H_2O$ shows the manganese ion to have a distorted octahedral environment[63]. The reaction of orthohydroxyacetophenone-picolylhydrazone $[H_2L]$ with $Mn(O_2CMe)_3.3H_2O$ has been reported to be pH dependent. Under conditions of low pH it gives a tetragonal monomeric complex $[Mn(HL)(O_2CMe)_2]$ (Fig. X) while under conditions of high pH, a dimeric tetragonal complex $[\{Mn(L)(O_2CMe)\}_2]$ (Fig. XI) is formed. However, orthohydroxyacetophenoneisonicotinoyl hydrazone (H_2Q) at low pH, gives a trigonal bipyramidal monomeric complex, $[Mn(HQ)(O_2CMe)_2]$ (Fig. XII), but under conditions of high pH, a square pyramidal dimer $[Mn(Q)(O_2CMe)_2]$ (Fig. XIII) is isolated. The spectral and magnetic properties of all the four complexes have been reported[64].

Thiols such as cysteine and penicillamine can stabilise a gold(III) to gold(0) complexes[65,66]. A kinetic study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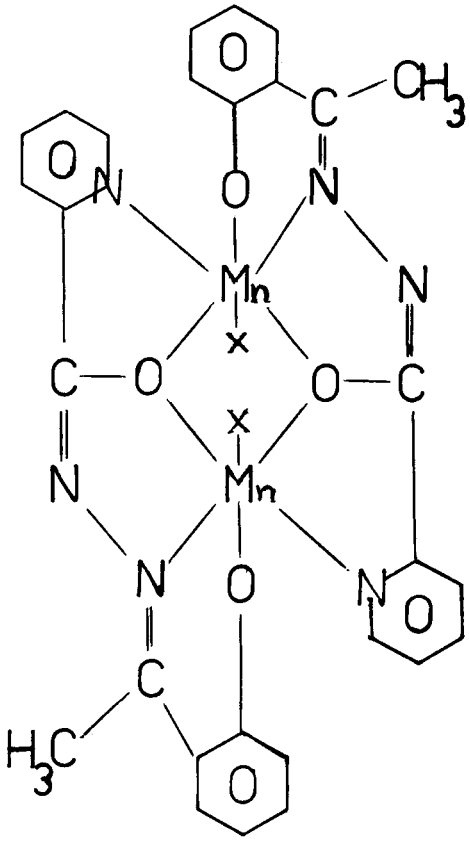
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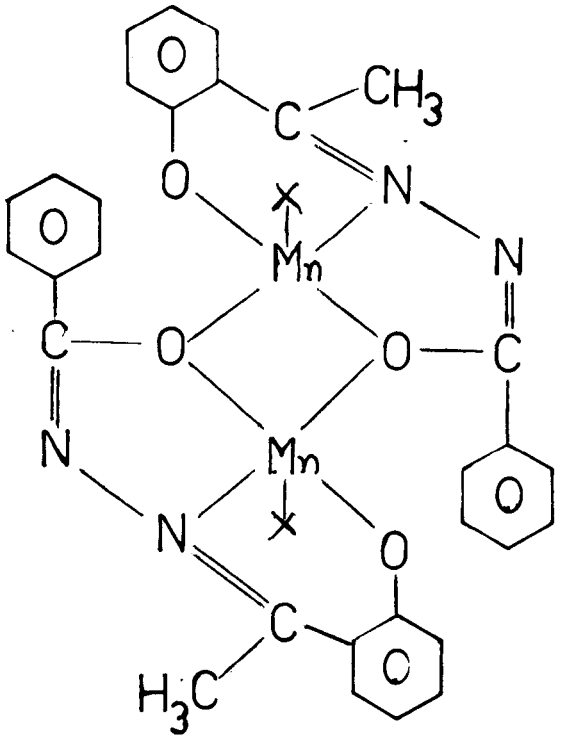
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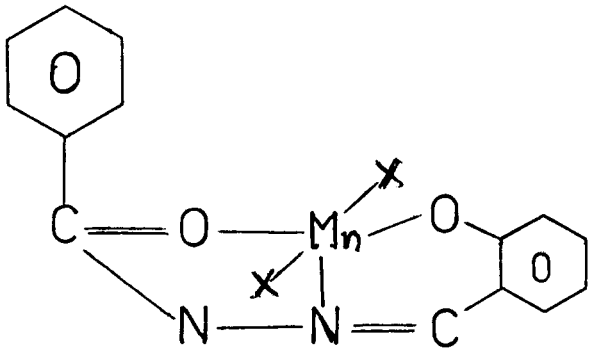
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confirms a two stage reduction of gold(III) to gold(I) with thioethers[67]. Reduction of gold(III) to gold(0) is also done with a disulphide such as dipenicillamine[68]. The reaction of $Hg(O_2CMe)_2$ with the ligand (Fig. XIV), after treatment with HCl, resulted in the formation of the complex, [HgLCl](HL = Fig. XV)[69]. A number of cysteine complexes of Hg(II) including [Hg(cys)Cl], $[Hg_2(cys)_3]$, $[Hg(cys)_2]$ and $[Hg_2(cys)_2Cl]$ have been characterised by IR and ESCA measurements[70]. The reaction of $HgCl_2$ with $Na(Et_2dtc)$ produces $[Hg(Et_2dtc)_2]_2$ and $[Hg_3(Et_2dtc)_4Cl_2]$. The trimetallic compound consists of polymeric chains with three different types of distorted tetrahedral mercury sites[71] (Fig. XVI).

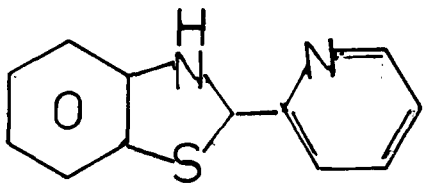


Fig. XIV

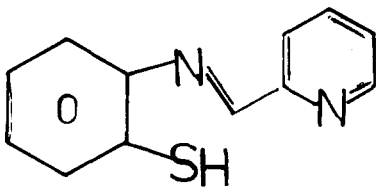


Fig. XV

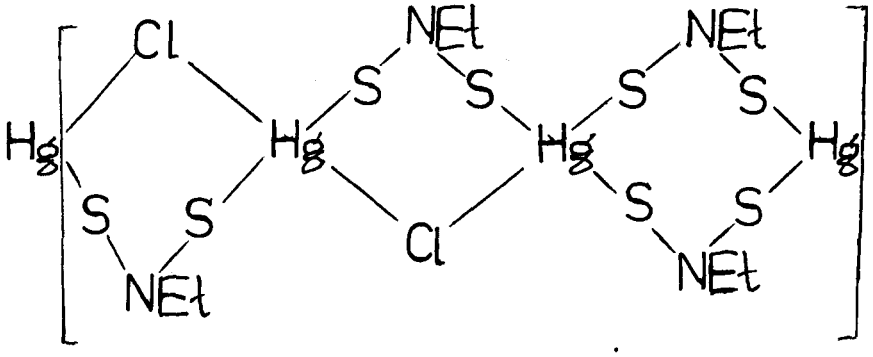


Fig. XVI

The first reported example of stable transition metal BH_4^- complex is $Mo(CO)_4BH_4^-$ where the formal oxidation state of the metal is zero. Interesting fluxional behaviour[72,73] have been shown by a variety of metal complexes incorporating BH_4^- unit as a ligand[72,74]. The addition of $Cu(CO)[HB(ps)_3]$ to a benzene solution of $MoH_2(C_5H_5)_2$ has resulted in a pale yellow product crystallised out within a few minutes. Analyses are consistent with the formula $(C_5H_5)_2\ MoH_2Cu[HB(ps)_3]$ while the mass spectrum contains peaks arising from $[Cu_2\ HB(ps)_3\ _2]^+$ and $[MoH_2(C_5H_5)_2]^+$. The most likely structure for this complex contain a dative molybdenum to copper bond[75] (Fig. XVII).

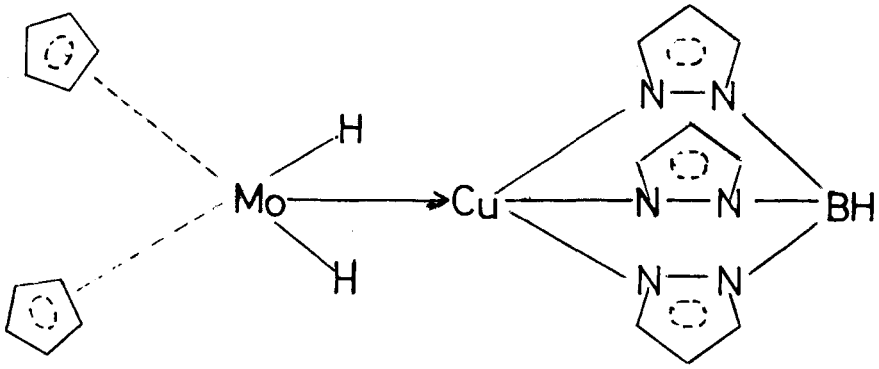
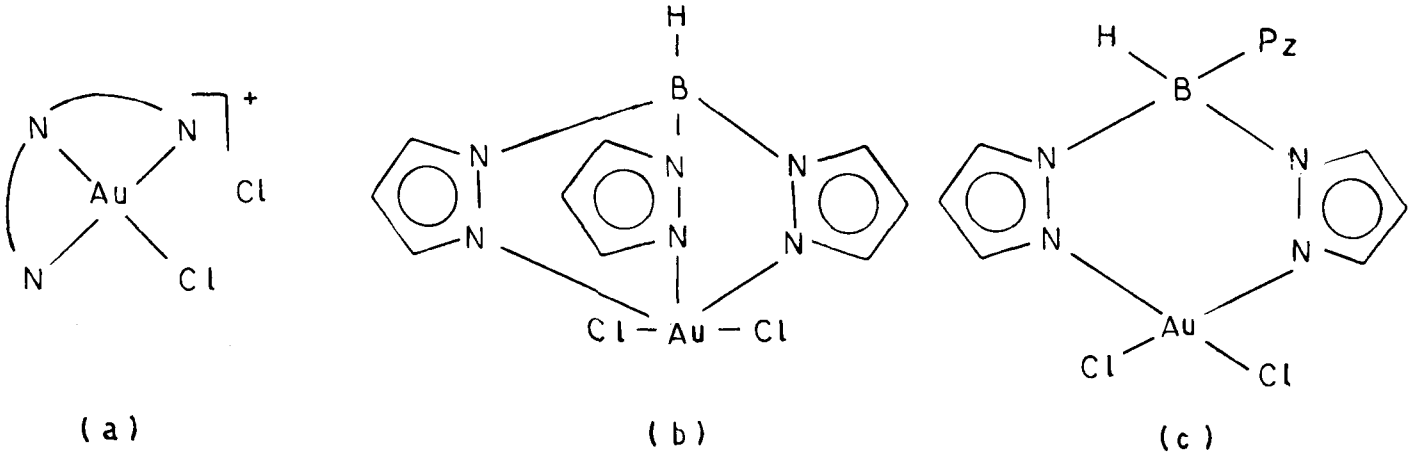


Fig. XVII

Molecular- and crystal structures of bis[dihydrobis-(1-pyrazolyl)-borato]Co(II)($[H_2B(ps)_3]_2Co$) have been determined by X-ray diffraction method. Its crystal structure consists of a packing of a discrete molecule which has two bidentate dihydro(1-pyrazolyl)bora

ligand [$H_2B(Pz)_2$] bonded to Cobalt(II). The metal was essentially tetrahedrally coordinated but a distortion from regular tetrahedron was also suggested[76]. Several possible formulations for the complex, $AuCl_2[(Pz)_3BH]$ were discussed. If all the three nitrogens are coordinated to gold, structures XVIIIa and XVIIIb are possible. The ionic structure XVIIIa was ruled out by conductivity measurements in nitrobenzene. In addition, it is not possible for the poly(pyrazolyl)borate to occupy three positions of the square plane expected for gold(III). In XVIIIb, both chlorines are coordinated to gold to give a five coordinated $AuCl_2$(N-N-N) complex which would be expected to have a distorted square pyramidal or trigonal bipyramidal geometry.



(a) (b) (c)

FIG. XVIII

PRESENT WORK

The present work deals with the syntheses and characterisations of tetramethylenedithiocarbamate(ATDC)-, β-naphthylaminedithiocarbamate(NADC)-, 2-mercaptobensothiasolylborate(2-MBT-yl) and 2-amino-5-mercapto-1,3,4-thiadiasole (AMTDA) complexes with transition metal ions.

Studies on mono-and dithiocarbamate complexes[77-81] of transition metal ions are quite extensive. They have been studied in order to examine the nature of the dithiocarbamate groups in a complex. The ammonium tetramethylenedithiocarbamate has been used in the extraction of metal ions[82] such as cadmium, cobalt, copper, iron, lead and nickel. Its complexes[83] with niobium, molybdenum and tungsten metal ions have been shown to be octacoordinated on the basis of magnetic measurements, infrared- and electronic spectral studies. It is interesting to note that inspite of the geometrical resemblance of tris (thiocarbamato) iron (III) with tris (dithiocarbamato) iron (III), they have been reported to differ in their magnetic properties[84]. Iron (III) in the former complex is in high spin state while in the latter case a crossover situation between high-spin and low-spin state has been suggested.

Complexes of ammonium tetramethylenedithiocarbamate and β-naphthylaminedithiocarbamate with Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Cd(II) have been synthesised under this project. The ATDC complexes of divalent metal ions have been prepared by the action of the metal on the dithiocarbamates in 1:2 ratio in hot ethanol while in the case of Fe(III) a 1:3 metal: ligand ratio was maintained in the same solvent. The NADC complexes with the transition metal ions have been synthesized by the direct action of carbon disulphide and the metal halides on the β-naphthylamine. These complexes were synthesized with a view to studying the symmetrical and nunsymmetrical hebaviour of the dithiocarbamato ligand.

After Trofimenko's pioneering work on the pyrasolylborate complexes in 1966, a number of pyrasolylborate complexes with coinage-[85], actinide[86]- and transition metals[87] have been reported. It is interesting and noteworthy that several new iron (IV) complexes of N,N-disubstituted dithiocarbamates prepared by the reaction of tris(diethyldithiocarbamato) iron (III) complexes with boron trifluoride in the presence of air have been characterized by a number of physical methods[88] as tris(N,N-disubstituted dithiocarbamato) iron (IV)-tetrafluoroborates. Mix-valence complexes characterised as μ-bis(N,N-diethyldithiocarbamato)- bis(N,N-diethyldithiocarbamato) dicarbonyldiruthenium (II,III) tetrafluoroborate

have also been reported. The structure has been described as a bis chelated $Ru(dtc)_2$ moiety sharing two sulphur atoms bridging different dithiocarbamato ligands of a six coordinated $Ru(dtc)_2(CO)_2$ moiety[89]. Each ruthenium atom is appreciably distorted from ideal octahedral geometry.

NMR studies of a variety of five coordinated methylplatinum(II) acetylene complexes stabilised by tridentate poly(pyrazolyl) borate ligands indicate them to be trigonal bipyramidal with the acetylene constrained within the trigonal plane of the platinum and two equatorial pyrazolyl nitrogen atoms[90]. However an attempt to prepare complexes with the $[H_2B(Pz)_2]^-$ and $HB[3,5-(CH_3)_2Pz]_3^-$ were unsuccessful. Immediate reduction of platinum(II) to platinum metal occurred with the dihydrobis (1-pyrazolyl) borate ion. The hydrotris (3,5-dimethylpyrazolyl) borate ligand appeared to degrade when added to a solution of the methyl (1,5-cyclo-octadiene) platinum cation liberating 3,5-dimethylpyrazole. Indazolyl- and nitroindazolylborate complexes with several transition metal ions[91-93] have been reported. It has been shown on the basis of reflectance spectral studies and magnetic measurements that dihydrobis(indazolyl) borate forms a chlorine bridged dimeric compound with Cu(II) and a ligand bridged polymeric octahedral compound with Ni(II) and Mn(II) ions. It is also interesting to note that the nitro-group

in the nitro-indasolylborate did not coordinate with the metal ions.

In the present work a series of dihydrobis-, hydrotris- and tetrakis(2-mercaptobenzothiazolyl)borate complexes with Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) have been synthesised employing the latter method by refluxing 2-mercaptobenzothiazole with KBH_4 in dimethylformamide in varying ratios and subsequent addition of the metal salt which resulted in the formation of poly (2-mercaptobenzothiazolyl)borates of the metal.

There are various methods for studying the soluble complexes being formed in solution. Spectrophotometric method is employed where coloured complexes are formed in solution. pH-metric method of Calvin and Bjerrum as modified by Irving and Rossotti is useful in the determination of stability constants of soluble complexes. The stability constant for the Ni(II) complex with the tetradentate ligand ethylenebisbiguanide was measured at 25°C by spectrophotometric method[94]. Stability constants for the formation of divalent metal complexes with 2-naphthohydroxamic acids were determined by pH titration technique[95]. Stability constants of the uranyl ion formed in aqueous media with 2-hydroxybenzene arsonic acid and 2,4-dihydroxybenzene arsonic acid were also determined. Thermodynamic dissociation constants of the benzene arsonic acid

and 2,4-dihydroxybensene arsonic acid were evaluated by using the potentiometric and spectrophotometric[96,97] data. Edwards' equation using stability data was applied for the approximation of the standard electode potential of the hypothetical diaqua Gold (I) and tetra Gold (III) ions[98]. Stability constants of 2,5-dimercapto-1,3, 4-thiadiazole complexes with the lanthanide(III) ions and the free energy for the formation of the complex were also calculated on the basis of pH-metric studies[99].

In this work 2-amino-5-mercapto-1,3,4-thiadiazole complexes with some lanthanide (III) metal ions have been studied employing the method of Irving and Rossotti. The stability constants of the complexes formed in 50% aqueous ethanol medium were determined. The free energy, enthalpy and the entropy of the reaction were also calculated using standard equations.

CHAPTER II

EXPERIMENTAL

E X P E R I M E N T A L

Of all the physico-chemical techniques available for studying the complexes, a few have been employed in the present case.[99a] A brief outline of the methods used is discussed as under.

I. IR Spectroscopy

Infrared absorption spectra are commonly obtained by placing the sample in one beam of a double beam infrared spectrophotometer measuring the relative intensity of transmitted and therefore the absorbed light energy versus wavenumber. When the infrared light of the same frequency is incident on the molecule, energy is absorbed and amplitude of that vibration is measured. When the molecule reverse from the excited state to the original ground state, the absorbed energy is released as heat. The occurrence or non-occurrence of an infrared radiation is governed by the following selection rules.

(i) In order for a molecule to absorb infrared radiation as vibrational excitation energy, there must be a change in the dipole moment of the molecule as it vibrates.

(II) In absorption of the radiation, only transition for which change in the vibrational energy level is $\Delta V=1$ can occur, Since most of the transition will occur from the state V_0 to V_1 the frequency corresponding to this energy is called the fundamental frequency.

The frequency of certain groups of atoms is called group frequency. These frequencies are characteristics of the groups, irrespective of the nature of the molecule in which these groups are attached. The absence of any band in the appropriate region indicates the absence of that particular group in the molecule. The following few paragraphs appropriate for the discussions of the compounds described in the present work are presented hereunder.

N-H Stretching Vibration

It occurs in the region 3500-3300 cm^{-1} in dilute solutions. Two absorption bands occur due to symmetric stretch one at 3500 cm^{-1} and the other near 3400 cm^{-1}. Secondary amines show only a single N-H stretching absorption in dilute solution in the above mentioned region. The N-H frequency in aliphatic secondary amines occurs in the range 3490-3310 cm^{-1}. It shifts to lower values in the hydrogen bonding.

N-H Deformation Vibration

Four characteristic peaks should appear for NH_2 group in primary amines but the only definite assignment has been done in the case of scissoring vibration generally observed in the region 1650-1590 cm^{-1}[100]. Secondary aliphatic amines show an extremely weak band in the range 1650-1550 cm^{-1} due to -NH deformation.

C=N Stretching Vibration

A band in the region 1690-1640 cm^{-1} is attributed to C=N stretching vibrations in open chain system. The C=N absorption bands are difficult to identify for two reasons, firstly owing to the considerable change in intensity which follow changes in its environment and secondly because information available on the effects of conjugation in ring system is often conflicting and indecisive.

C=S Stretching Vibration

The C=S absorption is found to be sensitive to the nature of the surrounding structure but the relative effects of various substituents are not always the same. In some molecules notably the thioamides and thioureas, the thiocarbonyl stretching frequency is uncertain as there is complete mixing between the C=S stretching mode and the other vibrations of similar frequencies[101,102].

There have been also great uncertainty with regard to the assignment of the C=S stretching frequency in nitrogen containing compounds. The frequencies in these compounds vary in the wide range of 850-1570 cm^{-1}. In thiourea, two bands in the region 1080-730 cm^{-1} are found to have appearable contribution from the C=S stretching vibration[101].

C-S Stretching Vibration

It generally appears as a band of weak or moderate intensity in the range 720-570 cm^{-1}. In phenyl sulphonyl halides the C-S vibration is found between 715 and 706 cm^{-1}.

M-S Stretching Vibration

The metal sulphur stretching frequency is of particular interest as it gives a direct evidence for coordination through the sulphur atom. It appears in the low frequency region viz., 480-210 cm^{-1} range[103]. In many instances, two bands one of medium to strong intensity and another weaker band at 10-40 cm^{-1} lower than the stronger band are observed.

B-H Stretching Frequency

The BH_2 stretching absorption gives rise to a strong band in the region 2230-2460 cm^{-1} and -BH stretch appears as a single peak at about 2470 cm^{-1}.

M-N Stretching Frequency

The M-N stretching frequency is of particular interest since it provides direct information regarding the coordinate bond. It appears in low frequency region (600-200 cm^{-1}). The M-N stretching frequency depends on the following factors.

(1) Mass of the metal and ligand
(2) Coordination number of the metal ion
(3) Oxidation number of the metal ion
(4) Geometry of the complex
(5) Basicity of the ligand molecule
(6) Bridging or non bridging anions and
(7) Ligand field stabilisation energy.

M-X Stretching Frequency

The metal halogen frequencies, mostly M-Cl system and to a lesser extent M-Br and M-I systems appear below 600 cm^{-1} region. These frequencies generally increase as the oxidation number of the metal increases. In the halogen bridged molecules of the type M_2X_6, in which the metal atoms have a square planar configuration, four stretching modes mainly bridging with the MX system and four mainly associated with terminal M-X group are observed. The best

known examples of the ions of this type are, the $(Pt_2X_6)^{-2}$ and $(Pd_2X_6)^{-2}$ systems where X = Cl, Br or I. Complexes of the type $Rh_2X_2L_4$ in which a square planar bridge is involved, have been investigated by Adams and Chandler[104]. In these systems, the spectra are not complicated by terminal Rh-Cl frequencies and the assignment is thus reasonably certain. The copper atoms in Cu_2X_4-(pyridine -1-oxide)$_2$ are bridged by the pyridine -1-oxide molecule whereas the four halogens are all in the terminal position. In this complex a single band at 315 cm^{-1} with a shoulder at 325 cm^{-1} must be due to the terminal Cu-Cl stretching frequency.

II. Ultraviolet and Visible (ligand field) Spectra

In order to interpret the ligand field spectra of transition metal couplexes, the devise of energy level diagram based upon 'Russel Saunder Scheme' must be introduced. This has the effect of splitting the highly degenerate configuration into groups of levels having lower degeneracies known as "term symbols".

The orbital angular momentum of electrons in a filled shell vectorially add up to zero. Total orbital angular momentum of an incomplete 'd' shell electrons is obtained by adding L values of the individual electrons which are treated as a vector with the component 'ml' in the direction

of the applied field, thus

$$L = \sum_i ml_i = \begin{matrix} 0 & 1 & 2 & 3 & 4 & 5 & 6 \\ S & P & D & F & G & H & I \end{matrix}$$

The total spin angular momentum $S = \sum_i Si$ where Si is the value of the spin angular momentum of the individual electrons. The degenerate values of S has the spin multiplicity equal to S + 1. Thus a term is finally denoted as $^{(2)}L'$. For example, if S = 1 and L = 1, the term will be ^3P and similarly S = $1\frac{1}{2}$ and L = 3, the term will be ^4F.

In general, the terms arising from a d^n configuration are as follows

d^1	d^9	^2D									
d^2	d^8	^3F	^3P	^1G	^1D	^1S					
d^3	d^7	^4F	^4P	^2H	^2F	$^2D_{(2)}$	^2P				
d^4	d^6	^5D	^3H	$^3F_{(2)}$	^3D	$^2P_{(2)}$	^1I	$^1G_{(2)}$	^1F	$^1D_{(2)}$	$^1S_{(2)}$
d^5		^6S	^4G	^4F	^4D	^4P	^2I	^2H	$^2G_{(2)}$	$^2F_{(2)}$	$^2D_{(3)}$ ^2P ^2S

When L and S are both non-zero then coupling between them takes place giving rise to a resistent angular momentum denoted by the quantum number 'j' which may have values from L+S to L-S e.g. in the case of ^3P, (L=1 and S=1) and ^4F, (L=3 and S=$1\frac{1}{2}$) the positive values of j representing state arising from term splitting are 2, 1 and 0 and $4\frac{1}{2}$,

$2\frac{1}{2}$ and $1\frac{1}{2}$ respectively. Each state specified by 'j' is 2j+1 fold degenerate.

Another scheme called 'J-J coupling scheme' is used when spin orbital interactions are larger and the electron repulsion parameters decrease . Spin angular momentum of an individual electron couples with its orbital momentum to give an individual j for that electron. The individual js couple to produce a resultant J for the atom. The electronic transition taking place in an atom or ion are governed by certain selection rules.

1. Transitions between states of different multiplicity are forbidden.
2. Transitions involving the exitation of more than one electron are forbidden.
3. In a molecule, which has a centre of symmetry, transitions between two gerade or two ungerade states are forbidden.

Interelectronic repulsions within a configuration give the energies of the terms above the ground term.

The energies are function of two parameters related to the electron repulsion. The two parameters may be chosen in either the way of Condon and Shortly (F_2 and F_4) or in that of Racah (B and C) for d orbital electrons.

For the first transition series ions value of C/B is around 4.0 and B is about 1000 cm^{-1}.

The ligand field splitting due to cubic field can be obtained by consideration of group theory. Splitting of the states for octahedral as well as for tetrahedral symmetry can be represented as

S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$
G	$A_1 + E + T_1 + T_2$

and so forth.

Transitions from ground state to the excited state occur in accordance with the selection rules described. The energy level order of the states arising from the splitting of a term state for a particular ion in an octahedral field is the reverse of that for this ion in a tetrahedral field.

III. Magnetic Measurements

Substances behave several kinds of magnetism i.e. paramagnetism, diamagnetism, ferromagnetism or antiferromagnetism. Most of the compounds containing transition metal

ions are paramagnetic. Diamagnetism arises when the electron spin moment and orbital moment of individual electrons in closed shell electrons balance one another. Ferromagnetism and antiferromagnetism arise as a result of interaction between dipoles of neighbouring atoms.

When 'S' represents the spin quantum number 'g' represents gyromagnetic ratio, the ratio of the magnetic moment to the angular momentum and μ_S is the spin magnetic moment for a single electron in Bohr magneton ($1BM = \frac{eh}{4\pi mc}$) units then

$$\mu_S = g\sqrt{S(S+1)}\ BM$$

When there is no orbital angular momentum, there cannot be any orbital contribution to the magnetic moment. If the orbital motion makes its contribution to the magnetic moment, the experimental effective magnetic moment shall be higher than the spin magnetic moment and in this case the moment will be given by

$$\mu_{S+L} = \sqrt{4S(S+1)+L(L+1)}$$

where L is the orbital angular momentum quantum number.

If a substance is placed in a magnetic field of magnitude H, the flux B within the substance is given by

$$B = H + 4\pi I$$

where I is the intensity of magnetisation. The ratio B/H is called the magnetic permeability of material given by

$$B/H = 1 + 4\pi(I/H) = 1 + 4\pi K$$

K is called the magnetic susceptibility per unit volume or volume susceptibility. B/H is the ratio of the density of lines of force within the substance to the density of such lines in the same region in the absence of the sample. Thus the volume susceptibility of a vacuum is by definition zero since in vacuum B/H = 1.

When the magnetic susceptibility is considered on weight basis, the gram susceptibility (X_g) is used instead of volume susceptibility. The μ_{eff} value can then be calculated from the gram susceptibility multiplied by the molecular weight and corrected for diamagnetic value as

$$\mu_{eff} = 2.84\sqrt{X_g M^{corr} T} \quad BM$$

where T is the absolute temperature at which the experiment is performed.

Magnetic susceptibility may or may not be dependent on temperature as given by the Curie Law

$$X_g M^{corr} = C/T$$

where C is called the Curie constant. Generally, μ_{eff}

value seems to depend on temperature within a certain limit. The dependance is given by $\chi_M^{corr} = C/T-\theta$ where θ is the Weiss constant and this expression is known as Curie- Weiss equation.

IV pH Metric Studies

For the study of coordinations compounds, formed in solution, potentiometric method occupies a unique position. A brief description[104a] of this technique is given below

The Concept of pH

Extremely small changes in the hydrogen ion concentration may determine whether a metal will dissolve or a metallic salt or a protein will precipitate. Just like the conventional notation $pK = -\log K$, the pH is written as $pH = -\log [H^+]$ and $pOH = -\log [OH^-]$. This notation 'pH' was introduced by Sorenson in 1909 as an abbreviation of " power of hydrogen" . The pH is usually a positive number ranging from about 0(for 1M acid) through 7(for a neutral solution) to about 14 (for 1M alkali).

Physical Measurement of pH

The definition of pH given by Sorenson is

$$pH = -\log C_{H^+} \quad \ldots\ldots (1)$$

basic difficulty is that the conventional means of

measuring pH reflect changes in activity rather than concentration. Hence pH is defined in activity definition as

$$pH = -\log a_{H^+} \qquad \ldots\ldots(II)$$

The e.m.f. of a cell free from liquid junction potential, consisting of hydrogen electrode and a reference electrode is given by

$$E = E_{ref} - \frac{RT}{F} \ln a_{H^+} \qquad \ldots\ldots(III)$$

i.e.

$$E = E_{ref} + 2.303 \frac{RT}{F} pH \qquad \ldots\ldots(IV)$$

where E_{ref} is the potential of the reference electrode on the hydrogen scale. It follows, therefore,

$$pH = \frac{F(E-E_{ref})}{2.303\ RT} \qquad \ldots\ldots(V)$$

If the usual value for E_{ref} is employed in this equation to derive pH the results are found to be inconsistent with other determinations that are thermodynamically exact. To remove the inconsistency, a value for E_{ref} should be found such that its use in equation (V) gives pH values which are consistent with the known thermodynamic dissociation constants

$$pH = pK_a + \log \frac{B}{a-B} - A\sqrt{\mu} + C\mu \qquad \ldots\ldots (VI)$$

this equation in combination with equation (V) gives

$$\frac{F(E - E_{ref})}{2.303RT} = pK_a + \log \frac{B}{a-B} - A\sqrt{\mu} + C\mu$$

therefore,

$$E - \frac{2.303RT}{F}\left(pK_a + \log \frac{B}{a-B}\right) - A\sqrt{\mu}$$

$$= E_{ref} + \frac{2.303RT}{F} C\mu \qquad \ldots\ (VII)$$

By preparing a series of mixtures, at different total ionic concentration, of an acid, whose dissociation constant is known exactly, e.g. from observation on cells without liquid junction, and its salt, series of values for B and a-B are given. The e.m.f. of the cells consisting of a hydrogen electrode in this solution and a reference electrode are measured. A saturated solution of potassium chloride is used as a salt bridge between the experimental solution and the one contained in the reference electrode. The E values obtained in this manner, together with B and a-B, calculated from the known composition of the acid salt mixture and the pK_a of the acid, permit the left hand side of equation (VII) to be evaluated for a number of solutions of different ionic strengths.

Calculation of formation curves of metal complexes from pH titration curves in mixed solvents

The stiochiometric stability constant of a metal-ligand complex, ML_n, is given by

$$^{C}K_n = [ML_n]/[ML_{n-1}][L]$$

and that of ligand-proton complex, LH_j, is

$$C_{K_j^H} = [LH_j]/[LH_{j-1}][H]$$

the overall stability constants are respectively

$$C_{B_n} = C_{K_1} . C_{K_2} . C_{K_3} ..... C_{K_n}$$

and $$C_{B_j^H} = C_{K_1^H} . C_{K_2^H} . C_{K_3^H} ..... C_{K_j^H}$$

Let the total concentration of ligand, metal and dissociable hydrogen in the system be T_L, T_M and T_H respectively. Then for the " degree of the formation of metal ligand complexes",

$$\bar{n} = \frac{\text{total concentration of ligand bound to metal}}{\text{total concentration of metal}}$$

$$= T_L - (\text{concentration of ligand not bound to metal})/T_M$$

Similarly, for ligand proton complexes,

$$\bar{n}_A = \frac{\text{total concentration of proton bound to metal}}{\text{total concentration of ligand not bound to metal}}$$

$$= (T_H - [H] / (T_L - \bar{n} . T_M)$$

and,

$$pL = \log \sum_{j=0}^{j=j} C_{B_j^H} [H]^j / (T_L - \bar{n} . T_M)$$

Suppose the initial volume, V^O, the mineral acid concentration E^O, and the total ligand concentration, $T_L{}^O$, are the same in each titration and that volumes V', V" of alkali concentration N, are added to reach points Na', Na" then $E'' = V^O E^O/(V^O+V'')$ $Na'' = V'' N/(V^O+V'')$ and $T_L'' = V^O T_L^O/(V^O+V'')$. Similar equation can be obtained for E' and Na'.

Therefor,

$$\bar{n}_A = Y.T_L^O + \frac{(V'-V^*)(N+E^O)}{(V^O+V')} /T_L^O$$

If the initial volume V^O and concentration of acid E^O and of ligand T_L^O are the same in each solution and the volumes V" and V"' of alkali concentration N are added to reach the points Na" and Na"', then

$$\bar{n}''' = \frac{(V''' - V'')\{N+E^O + T_L^O (Y - \bar{n}A)\}}{(V^O+V'')\bar{n}_A''' T_M}$$

and

$$pL = \log_{10}\left[\sum_{j=0}^{j=j} C_j^n \left(\frac{1}{\text{antilog}}\right)^j/(T_L-\bar{n}.T_M)\right]$$

EXPERIMENTAL TECHNIQUES

In addition to the infrared- and electronic spectral studies magnetic- and conductivity measurements, the elemental analyses is also a must to be performed for the verification of the occurracy and genuinity of the complexes synthesized. The melting point and the solubility were also checked for these complexes.

Carbon and hydrogen were analysed on a Thomas CH-analyser-35 and for nitrogen on a Coleman analyser-29. Metal, sulphur and chlorine were analysed by conventional methods. For the metal estimation, a known amount of the complex was decomposed with a mixture of nitric-, perchloric- and sulphuric acid in a beaker. It was then dissolved in water and made up to a known volume so as to titrate it with EDTA or Eriochromme black T. For sulphur and chlorine estimation, a known amount of the sample was decomposed in a platinum crucible and dissolved in water with a little concentrated nitric acid. The solution was then treated with either silver nitrate or barium chloride solution. The precipitate was dried and weighed.

The infrared and far-infrared spectra were recorded on a Beckman IR-20 (4000-200 cm^{-1}) spectrophotometer in KBr.

The far-infrared region (625-200 cm^{-1}) was also recorded with Perkin-Elmer grating spectrophotometer model 621 in nujol. Diffuse reflectance spectra (950-200 nm) were recoreded on a Carl-Zeiss VSU-2P spectrophotometer using MgO as calibrant.

The magnetic susceptibility measurements were done at room temperature by a vibrating sample magnetometer model 155. Conductance measurement was also made at 25°C on a Systronics 302 conductivity bridge.

The solution study of the lanthanide (III) complexes was done with an Elico pH-meter model LI-10 at 25 and 35°C.

CHAPTER III

COMPLEXES OF AMMONIUM TETRAMETHYLENEDITHIOCARBAMATE AND β-NAPHTHYLAMINEDITHIOCARBAMATE WITH SOME TRANSITION METAL IONS.

COMPLEXES OF AMMONIUM TETRAMETHYLENEDITHIOCARBAMATE AND β-NAPHTHYLAMINEDITHIOCARBAMATE WITH SOME TRANSITION METAL IONS

E X P E R I M E N T A L

Ammonium tetramethylenedithiocarbamate (BDH) (m.p. 150°C) was used as such. β-Naphthylamine (BDH) (m.p. 111-12°C) was recrystallised from ethanol. The ethanol and carbondisulphide were purified by the conventional methods. All the metal chlorides (BDH) were used as received.

Preparation of sodium β-naphthylaminedithiocarbamate.

An ethanolic solution of β-naphthylamine was added dropwise to a mixture of sodium hydroxide and carbondisulphide. The mixture (1:1:1 molar ratio) was stirred well and warmed on a water bath. The precipitated solid was filtered, washed and dried under vacuo.

Preparation of complexes.

The metal dithiocarbamates may be synthesised by one of the following two methods.

(a) by insertion of the carbon disulphide group in the presence of an amine.

$$MCl_2 + 2CS_2 + 2R_2NH \longrightarrow M(R_2NCS_2)_2 + 2HCl$$

(b) by a replacement reaction, if the sodium salt of the dithiocarbamate is used.

$$2R_2NCS_2Na + MCl_2 \longrightarrow M(R_2NCS_2)_2 + 2NaCl.$$

The Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes of ammonium tetramethylenedithiocarbamate were synthesised by the second method. The metal chlorides dissolved in hot ethanol, were gradually added with stirring to ATDC solution in 1:2 molar ratio in each case except in $FeCl_3$ for which a 1:3 molar ratio was taken. The reaction in this case was instantaneous and yielded coloured complexes which were filtered, washed and dried over calcium chloride.

The syntheses of β-naphthylaminedithiocarbamate(NADC) complexes with Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Cd(II) metal ions were done by the first method. All the solutions were prepared in ethanol. β-naphthylamine was added dropwise to a mixture of the metal chloride and carbon disulphide in 2:1:2 molar ratio. The reaction mixture was

stirred for an hour and warmed for fifteen minutes. The solids thus obtained were filtered, washed with excess of hot alcohol and dried in vacuo. The yield was 68.71%.

The analyses of the carbon and the hydrogen were done on a Thomas CH-analyser-35 and that of nitrogen on a Coleman analyser-29. The infrared spectra (4000-200 cm^{-1}) were recorded on a Perkin Elmer-521 grating spectrophotometer. UV-Vis spectra were recorded on a Carl-Zeiss spectrophotometer model VSU-2P. The magnetic measurements were done on a vibrating sample magnetometer model 155 at room temperature. Conductivity measurements were done on a systronics conductivity bridge type-302.

RESULTS AND DISCUSSION

The complexes synthesised were of the type $M(ATDC)_{2-3}$ and $M(NADC)_2$ or $M(NADC)_2Cl$. They were fairly stable to air and moisture at room temperature. The Mn(II), Co(II) and Cd(II) complexes of β-naphthylaminedithiocarbamate were soluble in acetone whereas Fe(III) and Cu(II) complexes of ATDC were soluble in benzene. Only the Ni(II) complexes of β-naphthylamine was soluble in nitrobenzene. The analytical result, the colour and the melting point of the complexes are recorded in Table I and II. The molar conductance of the NADC complexes measured in acetone or nitrobenzene at room temperature showed

them to have covalent character.

Infrared spectral studies

Ammonium tetramethylenedithiocarbamate (XIX) and sodium β-naphthylaminedithiocarbamate (XX) have the following structures. In the β-naphthylaminedithiocarbamate complexes a broad band at 3410 cm^{-1} has been assigned to -NH stretching

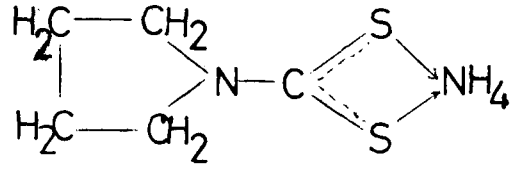


Fig. XIX

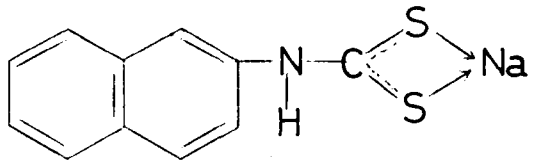


Fig. XX

frequency and another band at 1640 cm^{-1} to -NH deformation mode. There is, however, no change in the -NH absorption on going from the free NADC to the complexed ligand. This supports the noninvolvement of the -NH group in the coordination with the metal ions.

The study of the dithiocarbamate complexes is two fold. The dithiocarbamates have dual nature of acting both as a monodentate or a chelating ligand as has been observed in several cases[77-81]. Mode of bonding of the dialkyldithiocarbamates is well known[10]. There occurs a decrease in the >C=N double bond character after complexation as a consequence of which the C—N stretching frequency is usually lowered.

The lowering in νC=N is sensitive to the nature of the substituent on the nitrogen atom[106-108]. This frequency in aryldithiocarbamates appears in lower wave number region than in alkyldithiocarbamates due to the electron withdrawing nature of the aryl group as well as due to the negative charge on the sulphur atom.

The appearance of only a single strong C-S band around 1000 cm^{-1} suggests a symmetrical coordination of the dithiocarbamate group while for an unsymmetrically bound dithiocarbamate a doublet appears in the same range which are closely associated. The C-S bands are also influenced by the substituents on the nitrogen atom. For instance in a dialkyldithiocarbamate a single C-S band appears in 1000 $\pm$ 50 cm^{-1} whereas for a heterocyclic derivative, this band appears in 1000 $\pm$ 70 cm^{-1} region[109].

The tetramethylene and the β-naphthylamine groups have less tendency to release electrons to the nitrogen carbon bond and hence the double bond character between carbon and nitrogen was diminished. The C $\equiv$ N frequency in tetramethylenedithiocarbamate complexes as well as in β-naphthylaminedithiocarbamate complexes was observed in 1480-1440 cm^{-1} range. This was followed by another band around 1430 cm^{-1} in all the cases of ATDC complexes except for the Fe(III) complexes. These bands were intermediate between a

carbon-nitrogen double bond (1690-1640 cm^{-1}) and a carbon-nitrogen single bond (1360-1250 cm^{-1}) showing a partial double bond character.

Only one C=S absorption band was observed in 990-980 cm^{-1} in the case of ATDC complexes whereas in NADC complexes this band was observed in 1020-950 cm^{-1} range. These C=S absorption bands observed in the range of 1020-950 cm^{-1} in both the cases confirm the symmetrical coordination of the dithiocarbamate ligand[110,111].

The metal-sulphur stretching frequency in the ATDC complexes falls in the range 400-375 cm^{-1} and for those of the NADC complexes this band appears in the 480-420 cm^{-1} range which are in agreement with the values reported by Kwoka et al.[112]. Various other dithiocarbamate complexes of the transition metal ions have also been reported[110,113], to lie in 400-375 cm^{-1} region.

Electronic transitions and magnetic measurements

(I) Bis(tetramethylenedithiocarbamato) Mn(II) complex.

The colour of the complex and the spectral bands observed at 28,571 cm^{-1} and 25,641 cm^{-1} assigned to $^4E(G) \longleftarrow {}^6A_1$ and $^4A_1 \longleftarrow {}^6A_1$ transitions respectively are characteristics of a tetrahedral Mn(II) ion (Fig.XXI).

However, the μ_{eff} value (4.91 BM) is not very close to a tetrahedral Mn(II) ion but in view of the symmetry of the dithiocarbamate ligand a tetrahedral structure seems convincing.

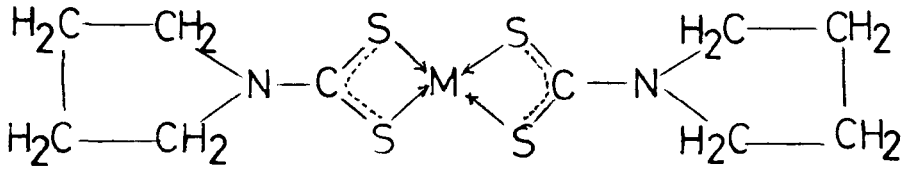


Fig. XXI.

(II) Bis(β-naphthylaminedithiocarbamato)Mn(II) complex.

It is known that Mn(II) ion in tetrahedrally coordinated environment has a magnetic moment value of 5.92 BM at room temperature. The μ_{eff} value of $Mn(NADC)_2$ complex (5.73 BM) is acceptable for tetrahedrally coordinated Mn(II) ion. The electronic transition with the $^6A_1$ as the ground term for Mn(II) ion is spin forbidden, probably due to spin-orbit interaction, this transition becomes two weak to be observed. When the Mn(II) ion assumed an octahedral configuration, the above band is seldom observed but in tetrahedral environment it often appears as a weak band[114]. The magnetic moment value of Mn(II) complex (5.73 BM), its pink colour and the weak electronic band at 19,417 cm^{-1} assigned to $^4T_1(G) \longleftarrow {}^6A_1$ are consistent with a tetrahedral geometry for Mn(II) ion.

(III) Tris(tetramethylenedithiocarbamato) Fe(III) complex.

The room temperature magnetic moment value (5.49 BM) of Fe(III) ion is intermediate between high and low spin state. This has been shown to have a thermal equilibrium between two magnetically isomeric forms[115,116]. The proton NMR spectra of iron-dithiocarbamates in other cases have also indicated the iron(III) ion to be in the intermediate crystal field of octahedral symmetry. The two strong charge-transfer bands at 34,500 and 28,571 cm^{-1} also support an octahedral geometry for iron (III) ion (Fig. XXIII).

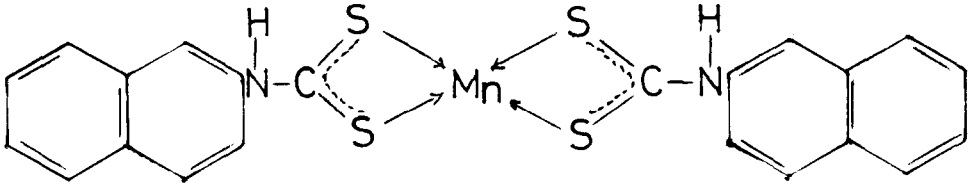


Fig. XXII.

(IV) Monochloro-bis(β-naphthylaminedithiocarbamato) Fe(III) complex

The black colour of the complex and the magnetic moment value of 6.1 BM corresponds to a high spin octahedrally

coordinated geometry for Fe(III) ion. In addition, the spectral bands at 18,550 cm^{-1} and 15,330 cm^{-1} assigned to $^4T_{2g} \longleftarrow {}^6A_{1g}$ and $^4T_{1g} \longleftarrow {}^6A_{1g}$ transitions, respectively also support the above stereochemistry for Fe(III) ion(Fig XXIV)

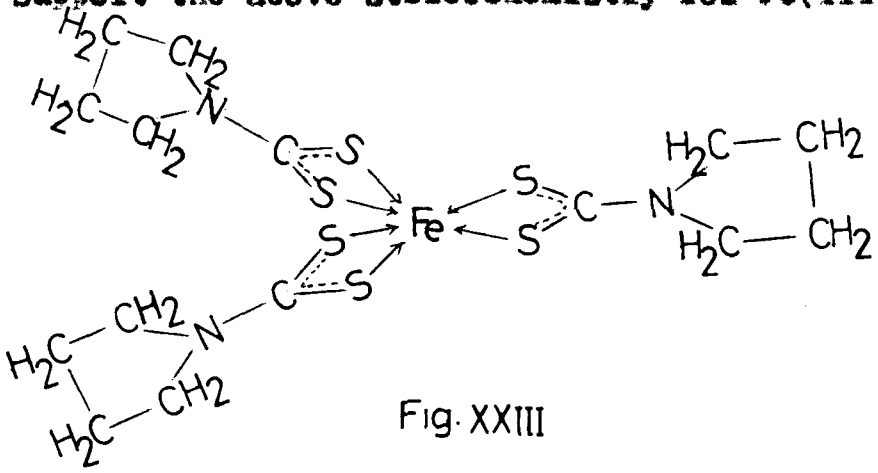


Fig. XXIII

(V) Bis(tetramethylenedithiocarbamato)Co(II) complex

The magnetic moment value in this case (4.17BM) is in the range normally accepted (3.90-4.42BM) for high spin Co(II) ion with tetrahedral configuration. The deep blue colour and the reflectance spectral bands at 14,705 cm^{-1}[116] also support the above configuration(Fig XXI)

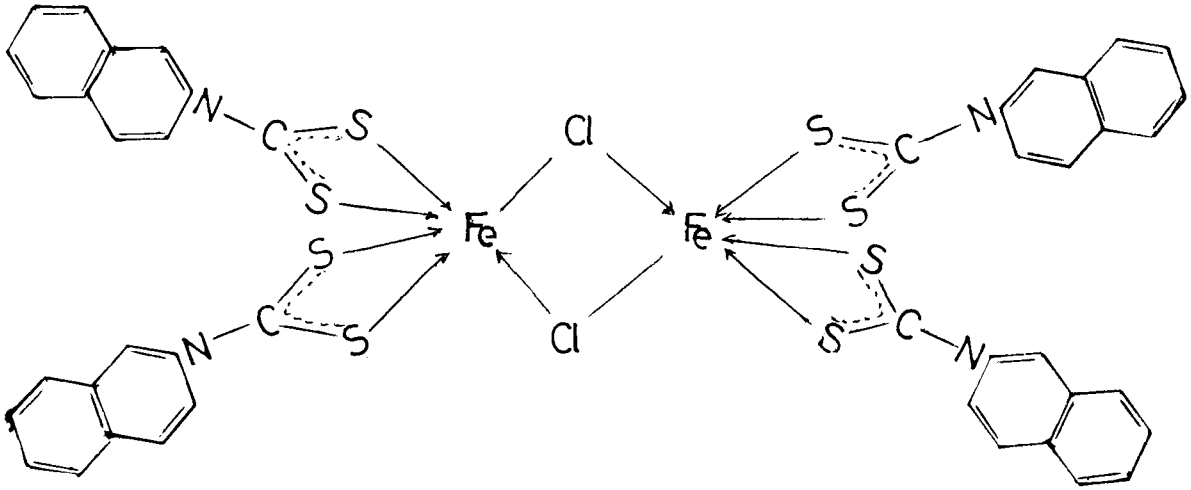


Fig. XXIV.

(VI) Bis(β-naphthylaminedithiocarbamato)Co(II) complex

A high spin square planar Co(II) ion is very rare[117], whereas the low spin square planar Co(II) complex is common having μ_{eff} value between 2.1-2.8 BM. In aqueous solution, Co(II) ion is usually oxidised[118] to Co(III). It has also been reported that in some cases the Co(II) ion does not undergo oxidation[119] during complexation, with ligands like dithiocarbamate even in aqueous medium. The possibility of the oxidation of Co(II) to Co(III) in this case is ruled out as all the solution used were non-aqueous and dry. Furthermore, the μ_{eff} value of 2.58 BM and the charge transfer band at 28,000 cm^{-1} (without the presence of any other band) also correspond[120-122] to a low spin square planar Co(II) (Fig XXV) complex. The μ_{eff} value also does not show the equilibrium between Co(II) to Co(III)

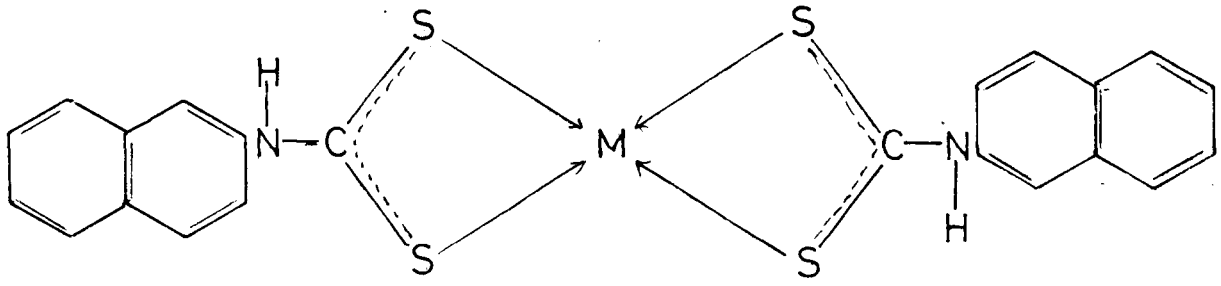


Fig. XXV (M = Co, Ni, Cu)

(VII) Bis(tetramethylenedithiocarbamato)Ni(II) complex

The absence of any band below 11,100 cm^{-1} and the presence of absorption bands at 15,625 cm^{-1} and 26,316 cm^{-1} assigned to $^1A_{2g} \longleftarrow {}^1A_{1g}$ and $^1B_{1g} \longleftarrow {}^1A_{1g}$ transitions respectively, are in favour of a square planar Ni(II) ion (Fig. XXV). The magnetic moment value in this case (0.9 BM) does not correspond to a diamagnetic Ni(II) ion with a square planar geometry, nevertheless such an anomalous magnetic moment value has been observed for diamagnetic Ni(II) ions in several cases[123-125]. This small magnetic moment value may be considered to be induced by the magnetic field which vanishes in the absence of the field.

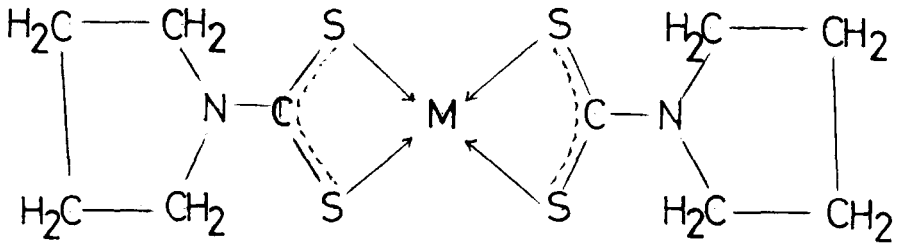


Fig. XXVI (M = Ni & Cu)

(VIII) Bis(β-naphthylaminedithiocarbamato)Ni(II) complex

The orange-red nickel(II) complex has the electronic spectrum indicative of a square plannr Ni(II) ion which does not display electronic bands below 10,000 cm^{-1}[126]. The band at 17,391 cm^{-1} may be assigned as V_1. This band is not always present in the spectra of square planar nickel(II)

complexes but is usually observed in the complexes with sulphur containing ligands[127]. The V_2 and the V_3 bands expected to appear in the range 23,000-20,000 cm^{-1} are both overlapped by the tail of a strong charge transfer band at 28,000 cm^{-1}. This complex gives a magnetic moment value of 1.86 BM. The paramagnetism may be due to an equilibirum between dia - and paramagnetic forms. Weak square planar crystal field also produce paramagnetism in Ni(II) complexes. In view of the observed magnetic moment and the composition of the complex tempts to believe that Ni(II) ions may be in the square planar environment (Fig.XXV).

(IX) Bis(tetramethylenedithiocarbamato)Cu(II) complex

The strong peak at 15,400 cm^{-1} accompanied by a shoulder at 13,100 cm^{-1} and magnetic moment value of 2.0 BM is indicative of a square planar configuration for Cu(II) ion (Fig. XXVI). It gives a magnetic moment of 2.1 BM. Spectral bands at 19,550 cm^{-1} and 15,152 cm^{-1} were assigned to $^2A_{1g} \longleftarrow {}^2B_{1g}$ and $^2B_g \longleftarrow {}^2B_{1g}$ transitions respectively.

(X) Bis(β-naphthylaminedithiocarbamato)Cu(II) complex

The reddish brown Cu(II) complex exhibits a magnetic moment value of 1.84 BM. The complex displays only one broad band in the visible region at 16,873 cm^{-1}. The charge transfer band with a strong tail above 20,000 cm^{-1}.would remain undetected

if the absorptions were weak. However, there are several square planar complexes which display two bands in 17,000-14,000 and 20,000-17,000 cm^{-1} [128] region. But the electronic spectrum of Cu(II) ion alone is not diagnostic of any stereochemistry. Considering the composition and the μ_{eff} value it is appropriate to assume a square planar configuration for this complex (Fig. XXV).

(XI) Bis(β-naphthylaminedithiocarbamato)Cd(II) complex.

No d - d transition is expected because of its configuration. On the basis of the limited studies, no suitable geometry could be assigned to this complex.

Thermogravimetric analysis of NTDC complexes

The thermograms showed that the Mn(II), Fe(III) and Cu(II) complexes decomposed at a temperature ($\sim$190°C) lower than the Co(II) and Ni(II) complexes ($\sim$280°C) losing one carbon disulphide molecule. The corresponding CoS and NiS residue were found at 360°C and 480°C respectively. The reaction may be represented by the typical equation as under:

$$M(C_4H_3NCS_2)_2 \longrightarrow MS + (C_4H_8N)_2\,C = S + CS_2.$$

TABLE - I

Physical Characteristics of Tetramethylenedithiocarbamate and β-Naphthylaminedithiocarbamate complexes

Complexes	Yield	Colour	Solubility	Melting point
$Mn(ATDC)_2$	45%	Yellow	Insoluble	260°C
$Mn(NADC)_2$	68%	Grey	Acetone	204°C
$Fe(ATDC)_3$	48%	Shining black	Benzene	170°C
$Fe(NADC)_2Cl$	68%	Black	Acetone	250°C
$Co(ATDC)_2$	49%	Black	Benzene	237°C
$Co(NADC)_2$	68.5%	Black	Acetone	202°C
$Ni(ATDC)_2$	52%	Yellowish green	Insoluble	300°C
$Ni(NADC)_2$	68.9%	Orange red	Nitrobenzene	250°C
$Cu(ATDC)_2$	49%	Brown	Insoluble	270°C
$Cu(NADC)_2$	70%	Reddish brown	D.D. Nitro-benzene	270°C
$Cd(NADC)_2$	71%	Slightly yellow	Acetone	decompose

TABLE - II

Elemental Analyses of Tetramethylenedithiocarbamate and β-Naphthylaminedithiocarbamate complexes

Complexes	%C		%H		%S		%N	
	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
$Mn(ATDC)_2$	34.5	34.12	8.06	8.07	36.88	37.08	4.61	4.44
$Mn(NADC)_2$	53.77	54.47	5.70	5.76	26.07	26.22	3.26	3.20
$Fe(ATDC)_3$	36.43	36.53	8.48	8.37	38.79	39.1	4.85	4.90
$Fe(NADC)_2Cl$	50.04	48.87	5.31	5.28	24.26 %Cl 6.64	24.31 6.66	3.03	3.06
$Co(ATDC)_2$	34.13	34.29	7.96	8.00	36.46	36.66	4.55	4.50
$Co(NADC)_2$	53.34	54.03	5.66	5.57	25.86	26.04	3.23	3.25
$Ni(ATDC)_2$	34.16	34.4	7.97	7.90	36.43	36.02	4.56	4.44
$Ni(NADC)_2$	53.36	53.61	5.66	5.47	25.87	25.83	3.23	3.01
$Cu(ATDC)_2$	33.8	33.7	7.86	7.56	36.06	36.54	4.49	4.50
$Cu(NADC)_2$	52.91	53.49	5.61	5.54	25.65	25.47	3.21	3.22
$Cd(NADC)_2$	48.14	48.10	5.11	5.06	23.34	23.40	2.92	2.90

TABLE - III

Some Important IR Frequencies of Tetramethylenedithiocarbamate and β-Naphthylaminedithiocarbamate Complexes

Complexes	IR Frequencies (cm^{-1})		
	(C - S)	(C = N)	(N - S)
$Mn(ATDC)_2$	980s	1450w	385w
$Mn(NADC)_2$	1020m	1440m	480s
$Fe(ATDC)_3$	980w	1450m	-
$Fe(NADC)_2Cl$	1020w	1470w	470w
$Co(ATDC)_2$	990m	1455m	385w
$Co(NADC)_2$	1010s	1440m	460w
$Ni(ATDC)_2$	990w	1455m	380w
$Ni(NADC)_2$	960s	1440s	460w
$Cu(ATDC)_2$	985m	1450m	385m
$Cu(NADC)_2$	950w	1460w	420w
$Cd(NADC)_2$	980s	1475m	460s

s stands for strong- m for medium- and w for weak band.

TABLE - IV

Electronic Transitions and Magnetic Moments of Tetramethylene-dithiocarbamate and β-Naphthylaminedithiocarbamate Complexes

Complexes	Wave Number (cm^{-1})	Assignments	Magnetic moments (BM)	Geometry
$Mn(ATDC)_2$	38,898 28,571 25,641	$^4E(G) \longleftarrow {}^6A_1$ $^4A_{1g} \longleftarrow {}^6A_1$	4.91	Tetrahedral
$Mn(NADC)_2$	28,600 19,417	$^4T_1(G) \longleftarrow {}^6A_1$	5.73	Tetrahedral
$Fe(ATDC)_3$	28,570 19,230 14,286	$^4T_2(D) \longleftarrow {}^6A_{1g}$ $^4T_{2g} \longleftarrow {}^6A_{1g}$ $^4T_{1g} \longleftarrow {}^6A_{1g}$	5.49	Octahedral
$Fe(NADC)_2Cl$	18,550 15,330	$^4T_{2g} \longleftarrow {}^6A_{1g}$ $^4T_{1g} \longleftarrow {}^6A_{1g}$	6.10	Octahedral
$Co(ATDC)_2$	22,727 14,705	Weak Band $^4T_1(P) \longleftarrow {}^4A_2$	4.17	Tetrahedral
$Co(NADC)_2$	28,000	Charge transfer	2.58	Square planar
$Ni(ATDC)_2$	26,316 15,625	$^1B_{1g} \longleftarrow {}^1A_{1g}$ $^1A_{2g} \longleftarrow {}^1A_{1g}$	0.9	Square planar
$Ni(NADC)_2$	28,000 17,391	Charge transfer $^1A_{2g} \longleftarrow {}^1A_{1g}$	1.86	Square planar
$Cu(ATDC)_2$	25,000 18,550 15,152	Charge transfer $^2A_{1g} \longleftarrow {}^2B_{1g}$ $^2E_g \longleftarrow {}^2B_{1g}$	2.13	Square planar
$Cu(NADC)_2$	28,600 16,873	Charge transfer $^2A_{1g} \longleftarrow {}^2B_{1g}$	1.84	Square planar

CHAPTER IV

SYNTHESIS AND CHARACTERIZATION OF THE POLY-(2-MERCAPTOBENZOTHIAZOLYL) BORATE COMPLEXES OF SOME TRANSITION METAL IONS.

SYNTHESIS AND CHARACTERISATION OF THE POLY (2-MERCAPTOBENZO-THIAZOLYL) BORATE COMPLEXES OF SOME TRANSITION METAL IONS:

E X P E R I M E N T A L

2-Mercaptobensothiazole and potassium borohydride (BDH) were used as received. Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) chlorides (BDH) were recrystallised. Dimethyl-formamide (E. Merck) was redistilled.

Preparation of the potassium dihydrobis(2-Mercaptobensothiasolyl) (2-MBT-yl)borate

A mixture of potassium borohydride (0.25 gm) and 2-mercaptobensothiasole (1.5 gm) in dimethyl formamide was refluxed for 12 hours at controlled temperature. The reaction proceeded instantaneously with the evolution of hydrogen gas which was collected over water. The amount of the gas collected was nearly equal to the calculated quantity of hydrogen. Refluxing was continued till the gas ceased to evolve. The contents of the flask turned into a yellow jelly like colloidal mass. The colloidal form of the mercaptobenzo-thiasolylborate formed in solution could not be filtered and isolated as it decomposed. The reaction can be represented as

$$KBH_4 + 2C_6H_4CSS.NH \longrightarrow K^+[H_2B(C_6H_4NCSS)_2] + 2H_2.$$

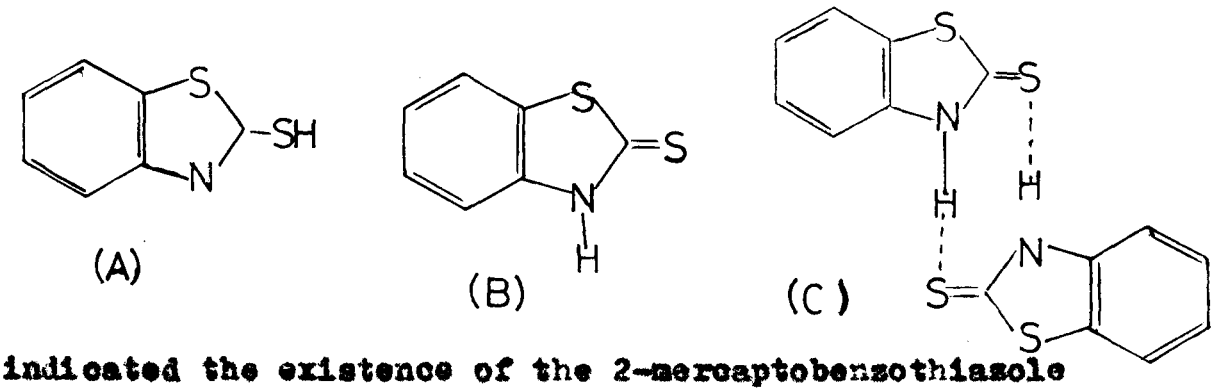
Preparation of the Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes of the pot. dihydrobis (2-MBT-yl)borates.

The above ligand solution was taken for the preparation of the metal complexes. A 1:2 metal chloride:ligand molar ratio was taken in each case except for $FeCl_3$ for which a 1:3 (metal chloride: ligand) molar ratio was used. The aqueous solution of metal chloride was added to the ligand solution with stirring. An immediate precipitation occurred with the evolution of heat. The precipitate thus obtained was warmed on a water bath. It was then dried in a vacuum desiccator. The yield ranges from 55-80%.

RESULTS AND DISCUSSION

2-Mercaptobenzothiazole exists in two tautomeric forms. Both the structures have been confirmed on the basis of its UV spectrum in benzene and chloroform. These structures are independent of the property of the solvent. Furthermore the structure (B) exists predominently[129,130] in equilibrium with a little quantity of the structure (A). However, an X-ray investigation has revealed the symmetrical bimolecular complex[131] (C) in the solid state indicating the intermolecular

hydrogen bonding between the H of the -NH group and S of the thioketo group. NMR and IR correlation data have also



indicated the existence of the 2-mercaptobenzothiazole mainly in the thioketo form (B). During the reaction with the metal ions this thioketo form is changed[132] into the thiol form though coordination takes place with the nitrogen heteroatom. The coordination through both nitrogen heteroatom and the mercaptide sulphur atom with Cu(II) metal ion has also been reported[133]. It is, therefore, interested to study the 2-mercaptobenzothiazolylborates with the expectation whether it forms a B-N or B-S bond.

The complexes of the dihydrobis(2-MBT-yl) borate with the Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) metal ions have been characterised by the elemental analyses, IR- and reflectance spectra and molar conductance-and magnetic measurement studies. They were fairly stable towards air and moisture, sparingly soluble in benzene, nitrobenzene and methanol but soluble in chloroform. The conductivity measurement of 1 x 10^{-3}M solution in chloroform showed the

non-ionic nature of the complexes.

Infrared spectral studies

In the IR spectra of the complexes of dihydrobis(2-MBT-yl)-borate, absorption bands characteristics[134,91,92] of (BH) are appeared in 2460-2380 cm^{-1} region. One of the two bands quoted at 1605 cm^{-1} and 1393 cm^{-1} is assigned[135] to B-N asymmetric band. In some of the nitrogen containing boron compounds, the B-N peak has been reported[136] to appear at 1113 cm^{-1}. If there is a partial double bond character[137], the B-N absorption band appears at 1520 cm^{-1}. A peak in the region 1090-1078 cm^{-1} appears persistently in the spectra of the metal(2-MBT-yl)borates while there is no absorption band in this region in the spectrum of free 2-MBT and hence assigned to B-N frequency. This frequency does not seem to be very sensitive to coordination. The absorption bands appearing in 420-380 cm^{-1} range assigned to M-N stretching frequency support the coordination of the metal through the nitrogen atom.

Electronic transitions and magnetic measurements

I. Bis[Dihydrobis(2-mercaptobenzothiazolyl)borato] Mn(II) complex

The magnetic moment for square planar Mn(II) ion in spin free state is expected to be 5.92 BM, while for spin paired configuration, the magnetic moment ranges from

1.75-2.2 BM. The magnetic moment value of 4.25 BM in the present case is lower than the spin free and greater than the spin paired moments. This intermediate value may, therefore,be regarded to be due to partial spin pairing as has also been observed in the manganous phthalocyanine complex[138]. The reflectance spectrum of the Mn(II) complex in this case shows the strong charge transfer bands at 40,816 cm^{-1} and 31,250 cm^{-1}. The band at 22,727 cm^{-1} is characteristic of a square planar Mn(II) ion with the ground term $^4A_{1g}$ $(b_{2g}^2, e_g^2, a_{1g}^1)$.

II. Tris[Dihydrobis(2-mercaptobenzothiazolyl)borato] Fe(III) complex

All the electronic transitions expected for the high spin Fe(III) ion are spin- and Laporte forbidden resulting in the occurrence of weak bands. Some of the bands are always confused with the charge transfer bands which begin to appear from the lower energy region. However in this case, a band observed at 27,027 cm^{-1} has been assigned to $^4T_{2g}(D) \longleftarrow {}^6A_{1g}$ transitions[139]. An appreciably strong band at 40,816 cm^{-1} with a weak band at 30,303 cm^{-1} are ascribed to be charge transfer bands. The room temperature magnetic moment value of 5.83 BM in this case is a little less than the calculated value for Fe(III) ion in the high spin state. The small decrease in the μ_{eff} value may be due

to slight antiferromagnetic effect. This magnetic moment value and the characteristic reflectance spectral bands support an octahedral environment for the Fe(III) ion.

III. Bis[Dihydrobis(2-mercaptobenzothiazolyl)borato] Co(II) complex

In the spectrum of dihydrobis(2-MBT-yl)borate Co(II) complex, the characteristic lowest energy band which gives Dq directly, [since $E(^4T_2)-E(^4A_2) = 10\ Dq$] has not been observed. In general, these weak bands are unobservable. Of the two bands to be observed in near infrared (5,000-8,000 cm^{-1}) and in visible region (13,000-16,600 cm^{-1}), only one broad band at 16,666 cm^{-1} followed by another weak band at 13,513 cm^{-1} has been observed. This band, assigned to $^4T_1(P) \longleftarrow {}^4A_2$ transition (Table VII) is in favour of the tetrahedral geometry for the Co(II) ion. The magnetic moment (5.11 BM) of the complex exceeds the normal value of 4.26-4.8 BM for the Co(II) ion in the tetrahedral environment which may be probably due to orbital contribution. Such a μ_{eff} value is not unusual[140] for the Co(II) ion in tetrahedral configuration.

IV. Bis[Dihydrobis(2-mercaptobenzothiazolyl)borato] Ni(II) complex

The reflectance spectrum of the Ni(II) complex shows no bands below 14,000 cm^{-1}. Two bands at 16,129 cm^{-1} and

22,727 cm^{-1} are assigned to $^1A_{2g} \longleftarrow {}^1A_{1g}$ and $^1B_{1g} \longleftarrow {}^1A_{1g}$ transitions respectively. The presence of the above band and the absence of any other bands below 14,000 cm^{-1} are characteristic of the Ni(II) ion in square planar environment. The magnetic moment value of 2.07 BM as against square planar diamagnetic Ni(II) ion have been supposed to involve an equilibrium between the diamagnetic and paramagnetic forms. Weak square planar crystal field having molecules in octahedral structure induces the positive increase[141] of χ the magnetic moment. Square planar structure[142,143] established by X-ray analysis of $NiS_4C_4Ph_4$, $[NiS_4C_4(CN)_4]^{-1}$ and $[NiS_4C_4(CN)_4]^{-2}$ having paramagnetism in the solid state also support this views.

V. Bis[Dihydrobis(2-mercaptobenzothiazolyl)borato] Cu(II) complex

The magnetic moment value (1.4 BM) in this case is fairly less than the spin only value (1.78 BM) for Cu(II) complexes. Such a low magnetic moment at room temperature was also reported for Cu(II) complexes[144]. This value of magnetic moment is simply because of the tendency to have tetrahedral configuration. The electronic transitions at 27,277 cm^{-1} in addition to the charge transfer bands, are also characteristic of the square planar configuration of Cu(II) ion.

TABLE - V

Physical Characteristics and Elemental Analysis of Dihydrobis(2-Mercaptobenzothiazolyl)borate Complexes

Character Analysis	$Mn(H_2BL_2)_2$	$Fe(H_2BL_2)_3$	$Co(H_2BL_2)_2$	$Ni(H_2BL_2)_2$	$Cu(H_2BL_2)_2$
Yield	55%	60%	65%	70%	80%
Colour	Dirty white	Light brown	Greenish blue	Steel grey	Light yellow
Solubility	Chloroform	Chloroform	S.S. Chloroform	Chloroform	S.S. Chloroform
Melting point	D	D	D	D	D
%C Cal.	45.10	46.20	44.86	44.87	44.58
%C Obs.	46.02	46.00	44.89	44.85	44.18
%H Cal.	7.52	7.70	7.47	7.48	7.43
%H Obs.	7.45	7.73	7.51	7.47	7.39
%S Cal.	34.36	35.19	34.17	34.19	33.97
%S Obs.	34.41	35.30	34.04	34.23	33.94
%H Cal.	2.69	2.75	2.67	2.67	2.65
%H Obs.	2.67	2.75	2.71	2.66	2.70

D stands for decompose.

TABLE - VI

IR Spectral Bands of Dihydrobis(2-Mercaptobenzothiazolyl)borate Complexes

Complexes	IR Frequencies (cm^{-1})			
	(B-H)	(B-N)	(C-S)	(M-N)
$Mn(H_2BL_2)_2$	2450w	1090m	1020m	380
$Fe(H_2BL_2)_3$	2455w	1080m	1030m	390
$Co(H_2BL_2)_3$	2440w	1090s	1020m	380
$Ni(H_2BL_2)_2$	2460w	1085s	1030m	
$Cu(H_2BL_2)_2$		1090w	1020m	

m stands for medium, s for strong, and w for weak bands.

TABLE - VII

Electronic Transitions and Magnetic Moments of the Dihydrobis(2-Mercaptobenzothiazolyl)-Borate Complexes

Complexes	Wave Number (cm^{-1})	Assignments	Magnetic Moments (BM)	Geometry
$Mn(H_2Bt_2)_2$	40,816 31,250s 22,727	Charge transfer	4.25	Square planar
$Fe(H_2Bt_2)_3$	40,816s 30,303s 27,027	Charge transfer $^4T_{2g}(D) \longrightarrow {}^6A_{1g}$	5.83	Octahedral
$Co(H_2Bt_2)_2$	37,037 16,666 13,513 sh,v.w.	Charge transfer $^4T_1(P) \longrightarrow {}^4A_2$	5.11	Tetrahedral
$Ni(H_2Bt_2)_2$	37,037 30,303s 22,727m 16,129m	Charge transfer $^1B_{1g} \longrightarrow {}^1A_{1g}$ $^1A_{2g} \longrightarrow {}^1A_{1g}$	2.07	Square planar
$Cu(H_2Bt_2)_2$	37,037 27,277 23,809	Charge transfer $^2A_{1g} \longrightarrow {}^2B_{1g}$	1.40	Square planar

Preparation of Potassium hydrotris(2-Mercaptobansothiasolyl)-borate.

Potassium borohydride (0.25 gm) was mixes well with 2.25 gm of 2-mercaptobensothiasole. The mixture was then refluxed using dimethylformamide as the solvent medium for 18 hours at controlled temperature. Hydrogen gas started to evolve as the brisk reaction with the dissolution took place. The evolving hydrogen collected over water (344 ml) ceased to evolve and still the refluxing continued till the contents of the flask turned into a thick liquid. This liquid was used for the preparation of the metal complexes. The reaction is represented as under:

$$KBH_4 + 3C_6H_4NCS.SH \longrightarrow K^+[HB(C_6H_4NCS)_3]^- + 3H_2$$

Preparation of the Mn(II), Co(II), Ni(II) & Cu(II) complexes of the pot. hydrotris(2-MBT-yl)borate

The divalent metalchloride and the ligand were taken in a 1:2 molar ratio. When the metal chloride solution was added with stirring into the ligand solution, there were an immediate precipitation with the evolution of heat. The container with the precipitate were warmed on a water bath for half an hour, filtered and washed repeately with water. It was dried in a vacuum desiccator. The yield ranges from 45-70%.

RESULTS AND DISCUSSION

The complexes of the hydrotris(2-MBT-yl)borate with the Mn(II), Co(II), Ni(II) and Cu(II) metal ions have been characterised by the elemental analyses, IR and reflectance spectra and molar conductance and magnetic measurements studies. All the complexes were fairly stable towards air and moisture. They were sparingly soluble in carbon tetrachloride but completely soluble in chloroform. Conductivity measurement of 1 x 10^{-3}M solution in chloroform revealed the neutral nature of the complexes.

Infrared spectral studies

The IR spectra of the hydrotis(2-MBT-yl)borate complexes showed the characteristic[134] bands of BH stretching frequency at 2400-2430 cm^{-1} region. The range in this case seemed to be quite narrower than the range found in the dihydrobis (2-MBT-yl)borate complexes. The BN stretching frequencies are observed at 1078-1080 cm^{-1} which is also within the range appeared in the cases of the complexes of the dihydrobis (2-MBT-yl)borate of the metal ions. The change in the position of the BN due to the metal ion coordination through the heteroatomic nitrogen atom was not significant. The other bands such as ring stretching at 1640-1660 cm^{-1} and the characteristic C = S band at 1035-1020 were found to be

virtually unchanged. Metal ion coordination through the nitrogen atom was indicated by the appearance of bands at 380-390 cm^{-1} assigned to νM-N.

Electronic transitions and magnetic measurements

I. Bis[Hydrotris(2-mercaptobenzothiazolyl)borato] Mn(II) complex.

The magnetic moment value of 5.72 BM in this case is slightly less than the calculated value of 5.92 BM for a d^5 Mn(II) ion in the octahedral configuration. This decrease is probably due to spin-orbit coupling.[145]. The reflectance spectrum shows strong bands at 38,461 and 31,250 cm^{-1} which are charge transfer bands. The other bands at 14,285 cm^{-1} and 11,904 cm^{-1} are assigned asymmetric bands because of the spin-orbit coupling nature of this ions. On the basis of the above discussions, an octahedral geometry is proposed for the $Mn(HBl_3)_2$ complex (Fig.XXVII).

II. Bis[Hydrotris(2-mercaptobenzothiazolyl)borato] Co(II) complex.

The magnetic moment value (2.94 BM) is greater than the normal value 2.1 to 2.8BM for low spin type square planar Co(II) complex. This value is much less than the value of the high spin octahedral Co(II) ion. This value can be

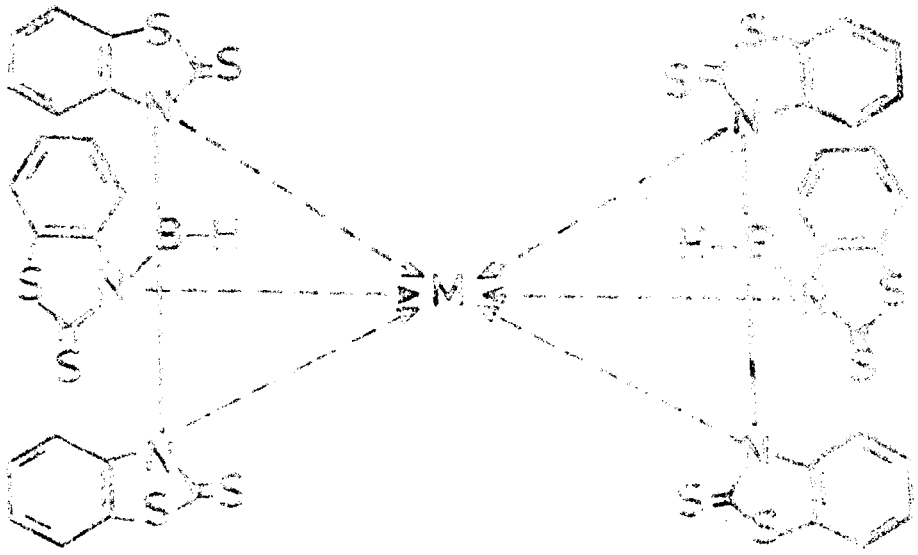


Fig. XXVIII M = Mn(II), Co(III) or Ni(III)

suggested due to the distortion of the octahedral environment leading to a square planar octahedral equilibrium[146]. The reflectance spectral band, at 16,666 cm^{-1} with two weak bands at 26,315 and 22,729 cm^{-1} also support the above geometry.

III. Bis[Hydrotris(2-mercaptobenzothiazolyl)borato Ni(II) complex

Octahedral Ni(II) complexes have a magnetic moment ranging from 2.8-3.5 BM. In the present case a moment of 3.4 BM is exactly within the range normally accepted. The reflectance spectral band at 25,641 cm^{-1} assigned to $^3T_{1g}(P) \longleftarrow {}^3A_{2g}(F)$ is characteristic[147,148] of an octahedral Ni(II) ion (Fig.XXVII). The other band in the range 18,000-15,000 cm^{-1} was not observed since this was expected to be spin forbidden band. The charge transfer band at 31,255 cm^{-1} and 27,027 cm^{-1} were also observed as strong and weak bands respectively.

VI. Bis[Hydrotris(2-Mercaptobenzothiazolyl)borato] Cu(II) complex

For a d^9 configuration having one unpaired electron the magnetic moment should be 1.73 BM. The diamagnetism[149] (Table IX) of the $Cu(HBL_3)_2$ complex indicates involvement of metal - metal interaction of a dimeric complex (Fig.XXVIII). The two strong charge transfer bands at 37,735 cm^{-1} and 34,482 cm^{-1}

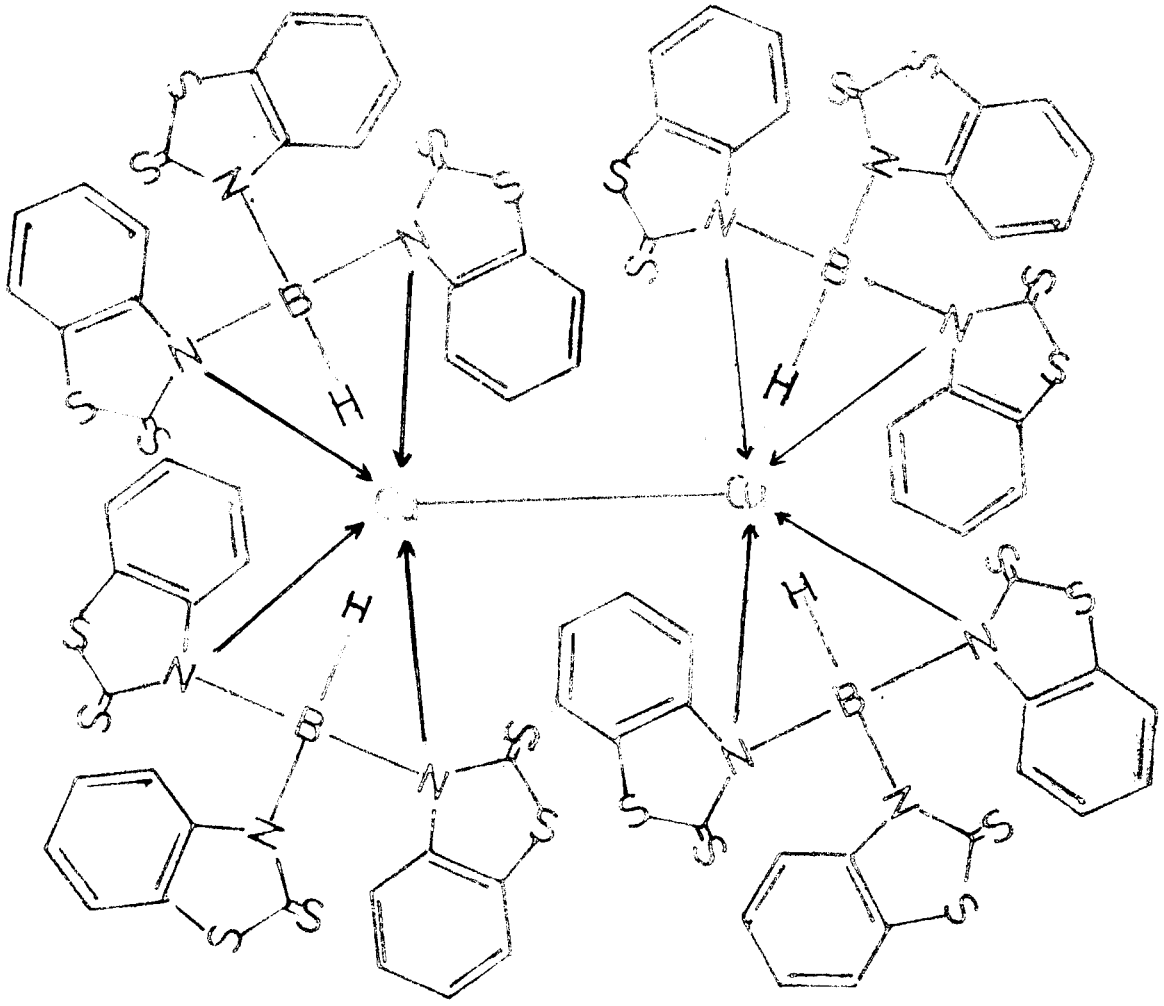


Fig. XXVIII

TABLE - VIII

Physical Characteristics and Elemental Analysis of Hydrotris(2-Mercaptobenzothiazolyl)borate Complexes

Character / Analysis		$Mn(HBL_3)_2$	$Co(HBL_3)_2$	$Ni(HBL_3)_2$	$Cu(HBL_3)_2$
Yield		48%	45%	50%	70%
Colour		Light yellow	Dark green	Yellowish green	Cream colour
Solubility		Chloroform & hot CCl_4	Chloroform	Chloroform	S.S. Chloroform
Melting point		Decompose	Decompose	Decompose	Decompose
%C	Cal.	46.88	46.71	46.72	46.51
	Obs.	46.79	46.60	46.81	46.7
%H	Cal.	7.81	7.78	7.78	7.75
	Obs.	7.90	7.77	7.76	7.77
%S	Cal.	35.72	35.58	35.59	35.44
	Obs.	35.59	35.32	35.60	35.46
%N	Cal.	2.42	2.41	2.41	2.39
	Obs.	2.53	2.38	2.42	2.40

TABLE - IX

IR Spectral Bands, Electronic Transitions and Magnetic Moments of Hydrotris(2-Mercaptobenzothiazolyl)-Borate Complexes

Complexes	IR Frequencies (cm^{-1})				Electronic Transitions		Magnetic Moments (BM)
	(B-H)	(B-H)	(C=S)	(M-N)	Wave Number (cm^{-1})	Assignments	
$Mn(HBL_3)$	2430w	1078w			38,461s 31,250s 14,285v.v. 11,904v.v.	Charge transfer	5.72
$Co(HBL_3)_2$	2400w	1080s	1035m	390	31,250s 26,315w 22,727w 15,360s	Charge transfer $^4A_{2g}(F) \longleftarrow {}^4T_{1g}(F)$	2.94
$Ni(HBL_3)_2$	2420w	1079m	1030m	380	31,255s 25,641 22,727w	Charge transfer $^3T_{1g}(P) \longleftarrow {}^3A_{2g}(F)$	3.4
$Cu(HBL_3)_2$	2420w	1080w	1020m		37,735s 34,482 24,027s	Charge transfer	Diamagnetic

m stands for medium-, s for strong- and w for weak bands.

were also observed in the reflectance spectrum[150]. Two other bands to be observed in respect of square planar configuration of Cu(II) ion in the range 15,000-20,000 cm^{-1} are also not visible.

Preparation of potassium tetrakis(2-Mercaptobensothiasolyl)-borate

0.25 gm of potassium borohydride was mixed well with 3 gm of 2-mercaptobensothiasole. The mixture was refluxed in dimethylformamide for 24 hours at controlled temperature. Reaction started as the mixture was put and refluxed into dimethylformamide. The hydrogen gas evolved was collected and measured to be 459 ml. The gases ceased to evolve but the refluxing continued till at last the contents were turned into yellow jelly like thick liquid which was used for the preparation of the metal complexes. Reaction can be represented as under:

$$KBH_4 + 4C_6H_4CSS.NH \longrightarrow K^+[B(C_6H_4CSSN)_4]^- + 4H_2$$

Preparation of the Mn(II), Co(II), Ni(II) and Cu(II) complexes of the pots. tetrakis(2-MBT-yl)borate

The above ligand solution was taken with the metal chloride in the 2:1 molar ratio. The metal chloride solution in water in each case was added to the ligand solution with

continuous stirring. The precipitate appeared immediately and that was digested on a water bath for about half an hour. The precipitate was filtered, washed with water and dried in a vacuum desiccator. The yield was 46-70%.

RESULTS AND DISCUSSION

The complexes of the tetrakis(2-MBT-yl)borate with the divalent metal ions e.g. Mn(II), Co(II), Ni(II) and Cu(II) were fairly stable towards air and moisture. They were found to be decomposing around 150-170°C. The complexes were characterised by the elemental analysis infrared and reflectance spectra, molar conductance and magnetic measurements studies. The conductivity measurement of the 1×10^{-3} M solution in chloroform of the complexes showed them to be neutral in nature.

The formation of the tetrakis(2-MBT-yl)borate and its complexes were characterised by the absence of the BH peak at the region 2380-2460 cm^{-1}. But a band characteristic of the BN stretching frequency was observed at 1065-1078 cm^{-1} region. In the case of Mn(II) tetrakis(2-MBT-yl)borates the BH peak was found to have a small decrease. The metal to nitrogen coordination was established by the M-N at 380-390 cm^{-1}

region. The ring stretching frequency at 1640-1660 and the C=S bands were found to have only small shifts.

Electronic transition and magnetic measurement

I. Bis[Tetrakis(2-mercaptobenzothiazolyl)borato] Mn(II) complex

The octahedral complexes of Mn(II) have a magnetic moment as high as 6.12 BM and as low as 5.6 BM. The μ_{eff} value of 5.8 BM in the present case cannot be consider a deviation from the octahedral μ_{eff} value[151]. The strong band at 31,250 cm^{-1} in the reflectance spectrum is a charge transfer band. A medium band at 26,021 cm^{-1} followed by another weak band at 16,129 cm^{-1} is assigned to $^4A_{1g}(G) \longleftarrow {}^6A_{1g}$ transition. These bands are in conformity[152] with an octahedral configuration of the Mn(II) ion in this complex (Fig. XXIX).

II. Bis[Tetrakis(2-mercaptobenzothiazolyl)borate] Co(II) complex

The magnetic moment value (5.36 BM) for Co(II) tetrakis-(2-MBT-yl)borate is less than the octahedral μ_{eff} value of 4.7-5.21 BM. This value may be supposed to be a little less than the tetrahedral magnetic moment value of 4.2 to 4.8 BM with the $^4A_2$ ground term. This may be due to some

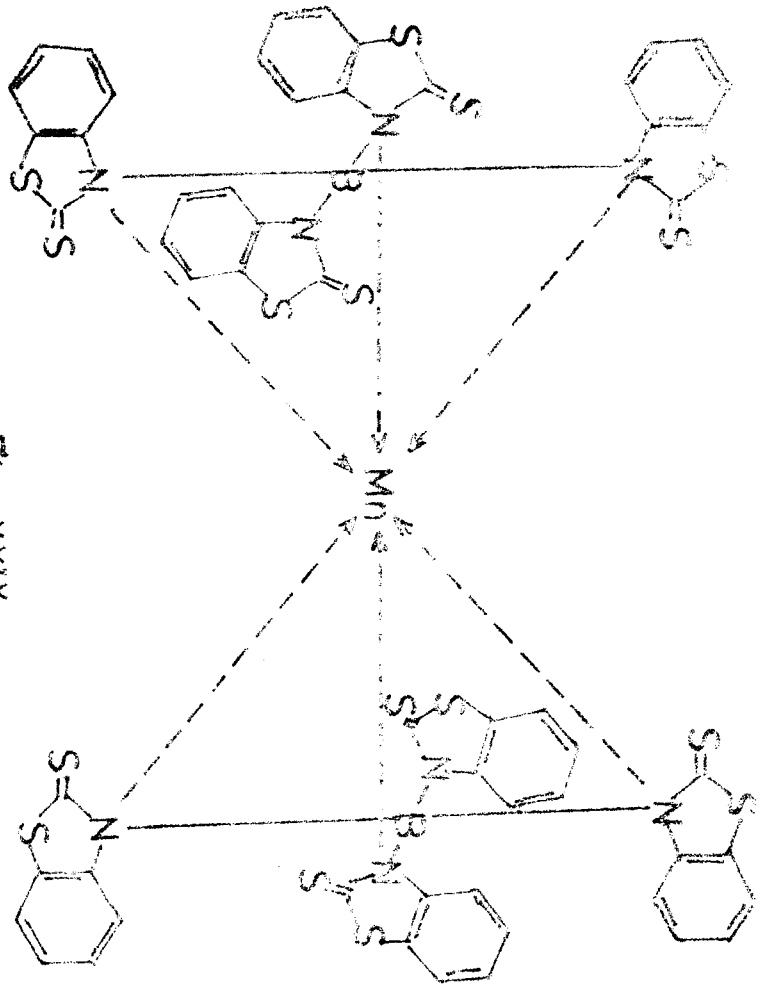


Fig. XXIX

square planar tetrahedral tendency of the Co(II) ion. The electronic spectral bands at 16,130 cm^{-1} and 13,513 cm^{-1} assigned to $^4T_1(P) \longleftarrow {}^4A_2$ and $^4T_1(F) \longleftarrow {}^4A_2$ are in support[116] of the tetrahedral geometry of the Co(II) ion (Fig. XXX).

III. Bis[Tetrakis(2-mercaptobensothiasolyl)borato] Ni(II) complex

Two weak bands in the ultravoilet region of the electronic spectrum are appeared with the strong charge transfer band at 31,250 cm^{-1}. A band characteristic of square planar Ni(II) ion has been observed at 22,727 cm^{-1} and assigned to $^1A_{2g} \longleftarrow {}^1A_{1g}$ transition. The diamagnetism[153] and the colour of the complex support the square planar geometry of the Ni(II) ion in the tetrakis(2-MBT-yl)borate complex.

IV. Bis[Tetrakis(2-mercaptobensothiasolyl)borato] Cu(II) complex

The Cu(II) complex has been found to be diamagnetic. Although the electronic spectral bands (Table XI) cannot be diagnostic of the stereochemistry of the complex, the μ_{eff} value seems to indicate some spin-spin interaction between the copper atoms.

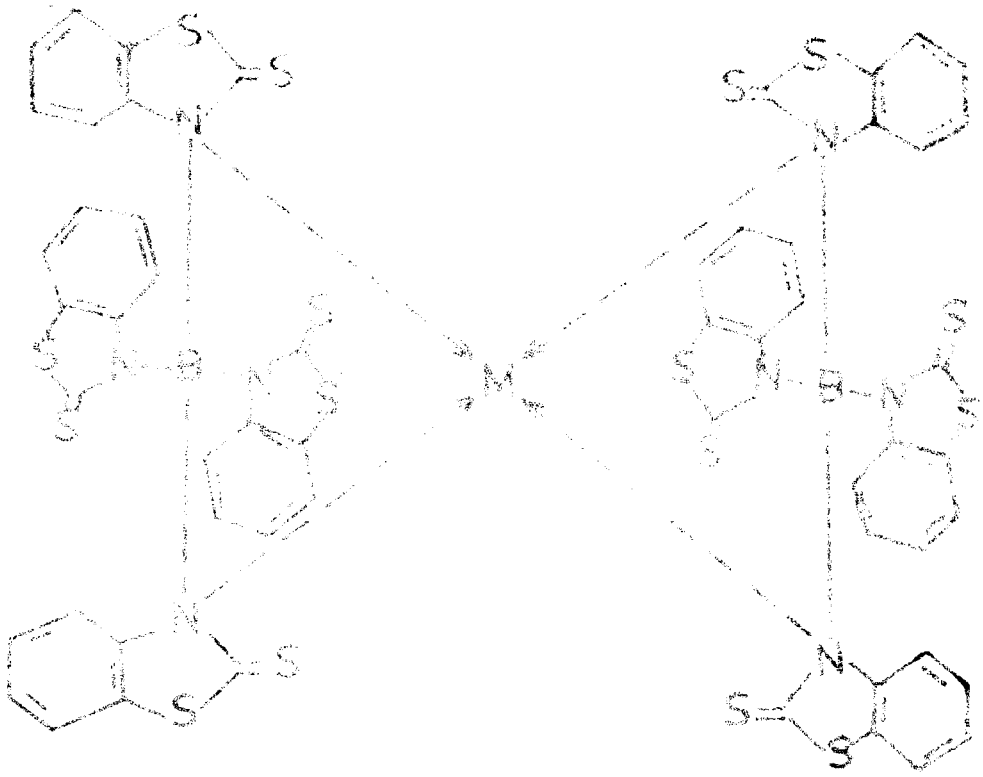


Fig. XXX. M = Co(II) or Ni(II)

TABLE - X

Physical Characteristics and Elemental Analysis of Tetrakis(2-Mercaptobenzothiazolyl)Borate Complexes

Character / Analysis		$Mn(BL_4)_2$	$Co(BL_4)_2$	$Ni(BL_4)_2$	$Cu(BL_4)_2$
Yield		48%	46%	50%	70%
Colour		Yellow	Dark green	Reddish brown	Orange yellow
Solubility		Chloroform & acetone	Chloroform	Chloroform	Chloroform & CCl_4
Melting point		Decompose	Decompose	Decompose	Decompose
%C	Cal.	47.83	47.69	47.70	47.54
	Obs.	48.21	48.27	49.00	48.45
%H	Cal.	7.97	7.95	7.95	7.92
	Obs.	8.01	7.88	7.79	7.99
%S	Cal.	36.44	36.34	36.34	36.22
	Obs.	36.62	36.39	36.28	36.41
%N	Cal.	2.27	2.27	2.27	2.26
	Obs.	2.25	2.19	2.28	2.19

TABLE - XI

IR Bands, Electronic Transitions and Magnetic Moments of Tetrakis(2-Mercaptobensothiazolyl)Borate Complexes

Complexes	IR Frequencies (cm^{-1})			Electronic Transitions		Magnetic Moments (BM)
	(B-N)	(C=S)	(M-N)	Wave Number(cm^{-1})	Assignments	
$Mn(BL_4)_2$	1078s	1030m	380	31,250s 26,021m 16,129w	Charge transfer $^4A_{1g}(G) \longleftarrow {}^6A_{1g}$	5.8
$Co(BL_4)_2$	1080s	1035m	390	38,461w 31,250s 16,247 13,513	Charge transfer $^4T_1(P) \longleftarrow {}^4A_2$ $^4T_1(P) \longleftarrow {}^4A_2$	3.4
$Ni(BL_4)_2$	1080s	1037m	385	38,461w 31,250s 22,527s	Charge transfer $^1A_{2g} \longleftarrow {}^1A_{1g}$	Diamagneti
$Cu(BL_4)_2$	1085s	1020m	390	38,461s 31,250s 28,571w	Charge transfer	Diamagneti

m stands for medium-, s for strong- and w for weaker band.

CHAPTER V

STABILITY CONSTANTS OF Nd(III), Sm(III), Gd(III), Tb(III) Dy(III) AND Ho(III) COMPLEXES OF 2-AMINO-5-MERCAPTO-1,3,4-THIADIAZOLE.

STABILITY CONSTANTS OF Nd(III), Sm(III), Gd(III), Tb(III), Dy(III) AND Ho(III) COMPLEXES OF 2-AMINO-5-MERCAPTO-1, 3,4-THIADIAZOLE.

E X P E R I M E N T A L

The ligand 2-amino-5-mercapto-1,3,4-thiadiazole, (m.p. 245, Koch-light) was taken as such. Nd(III), Tb(III), Dy(III) and Ho(III) chlorides were also taken as received whereas the Sm(III) and Gd(III) chlorides obtained from Sm_2O_3 and Gd_2O_3 were made anhydrous by standard technique[154]. The stock solution of the ligand was prepared by dissolving the requisite amount in ethanol. Sodium hydroxide and sodium perchlorate (Riedel) solutions were prepared in carbon dioxide free double distilled water. The sodium hydroxide and perchloric acid solutions were standardised by known methods[155].

An ELICO, LI-10 pH-meter having an accuracy of ± 0.05 unit was employed in combination with glass-calomel electrodes. The calibration of pH-electrode system was done with the help of standard buffers (pH 4.0 and 9.12). An inert atmosphere was maintained by bubbling oxygen and carbon dioxide free nitrogen gas, through the solution.

Calvin-Bjerrum pH-titration method

The Calvin-Bjerrum pH titration technique as modified by Irving and Rossotti was employed to study the stability constants[155a] of some rare earth metal ions with 2-amino-5-mercapto-1,3,4-thiadiazole. The following solutions containing (A) 5.0 ml of (0.10M) $HClO_4$; (B) 5.0 ml of (0.10M) $HClO_4$ + 25 ml of (0.005M) AMTDA; and (C) 5.0 ml of $HClO_4$ containing metal ions (0.005M) + 25 ml of (0.005M) AMTDA each diluted to a fixed volume (50 ml) with distilled water and kept at constant ionic strength (0.1M) by the addition of requisite amount of one molar sodium perchlorate solutions, were titrated against standard solution of sodium hydroxide (1.60×10^{-1}M).

The pH correction factor was determined for the conversion of the pH-meter reading (B) into hydrogen ion concentration at 50% V/V water ethanol-medium using the following technique.

The hydrogen ion concentration was determined according to Van Uitert and Haas's relationship[156]

$$- \log H^{+} = B + \log U_{H} \qquad - 1$$

where B is the pH-meter reading and $\log U_H$ is the pH correction factor in aqueous-ethanol mixture at a particular temperature and related to the activity coefficient according

to equation (2)

$$\log U_H = \log U_H^0 - \log (1/\gamma \pm) \qquad - 2$$

where $\log U_H^0$ is the the conversion factor and is independent of ionic concentration.

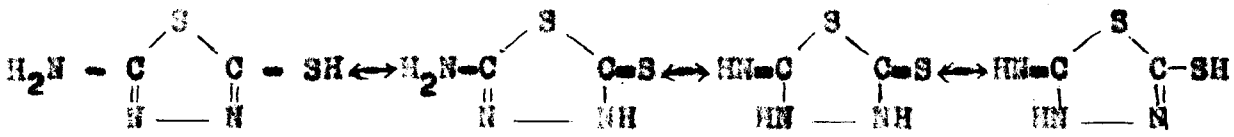
The value of $\log U_H$ for 50% v/v ethanol-water medium at a desired ionic strength were obtained by comparing pH-meter reading with the stoichiometric concentration during the titration of $HClO_4$ with tetramethylammonium hydroxide in 50%, v/v ethanol-water medium. The values of the activity coefficient, $\log (1/\gamma \pm)$ were determined by interpolation from the plot of $\log (1/\gamma \pm)$ against mean molarity ($m_\pm$) in 50% volume ethanol + 50% volume water from the data given by Scatchard[157] for HCl in aqueous-ethanol system. The negative logarithm of dissociation constant, pK_D can be calculated with the help of equation

$$pK_D = B + \log U_H + \log 1/\gamma \pm \qquad - 3$$

Proton-ligand stability constant.

Guha[158] proposed the name 2-thiol-5-amino-1,3,4-thiadiazole for the Freund's compound formerly known as dithiourazole. This could explain the unstability of the diacetyl compound towards a mild treatment e.g. boiling or slight heating, losing one of its acetyl group and

forming the stable monoacetyl derivative. This compound exist in four tautomeric forms[159].



Because of the role played by one labile hydrogen atom, two varieties of compounds, one melting at 245° and another melting at 234°, were found. IR band for the higher melting variety occurred at 3600-2500 cm^{-1} whereas for the lower melting variety it occurred 4200-3400 cm^{-1} region. This synchronised the monoprotic nature of the AMTDA by ionising one hydrogen atom as follows.

$$H_2NCN_2CS_2H \rightleftharpoons H_2NCN_2CS_2^- + H^+$$

Ionisation of the proton was also shown by the nature of the deviation of the acid ligand curve from the pure acid curve near pH-meter reading B=2.8 (Fig. XXXI). But no colour change took place as the B value increased. The proton-ligand formation number, n_A values were calculated by

$$\bar{n}_A = Y - \frac{(V_2-V_1)(N^0+E^0)}{(V^0+V_1)\ T_L} \qquad -4$$

where T_L = total ligand concentration, Y = total number of dissociable protons present in the ligand, N^0 = concentration of the alkali, E^0 = concentration of the mineral acid and

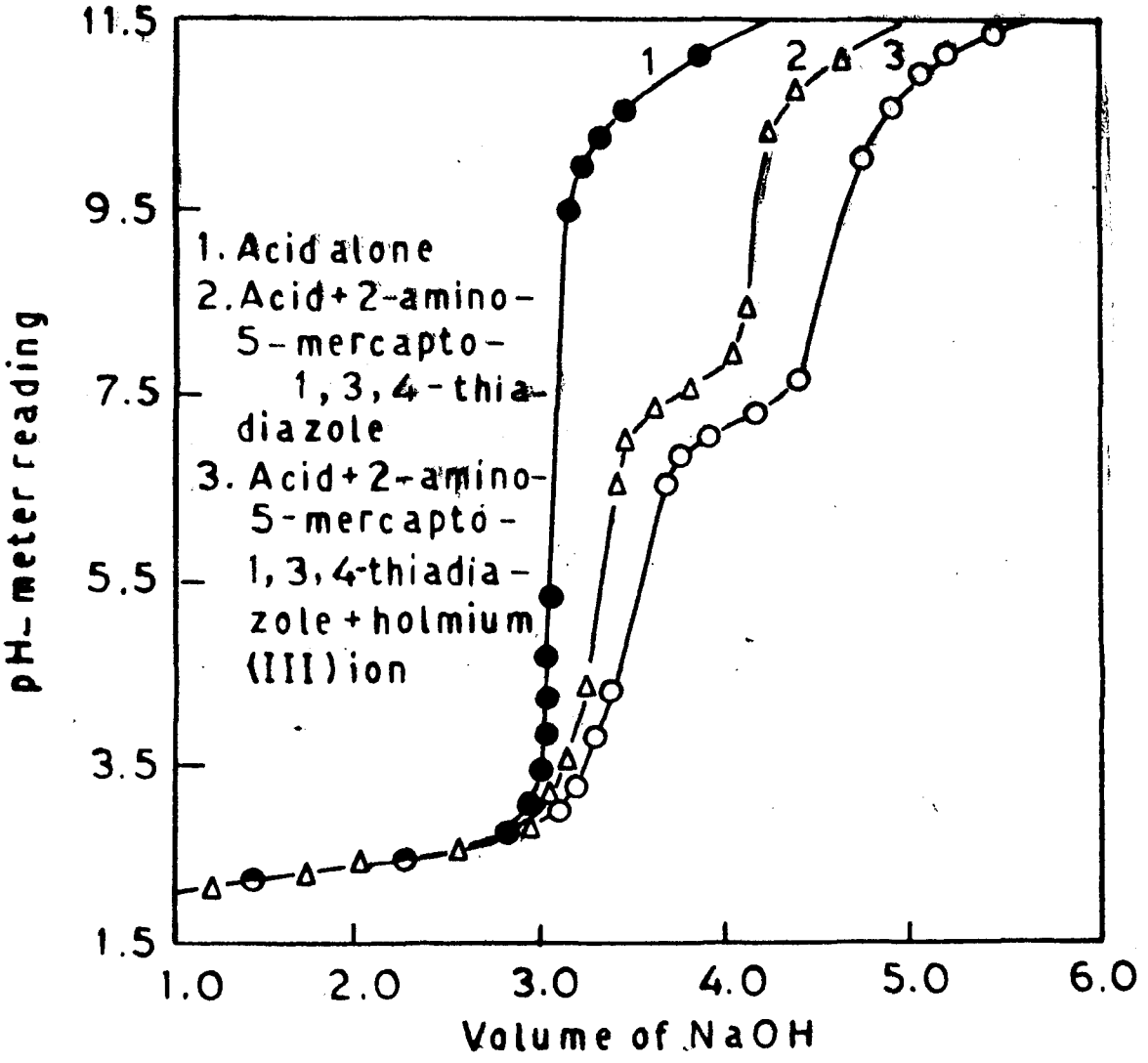


FIG. XXXI TYPICAL TITRATION CURVES OF RARE EARTH (III) ION COMPLEXES AT 25°C

V^0 = Total fixed volume. The highest $\bar{n}_A$ value was less than 1.4 (Table XII) showing thereby that 2-amino-5-mercapto-1,3,4-thiadiazole had only one ionisable proton which was released between B = 2.6 and 3.0.

$\bar{n}_A$ was plotted against B, to get the proton-ligand formation curve (1) (Fig. XXXII). The approximate value of the proton-ligand stability constants pK_1^H were obtained by half-integral method as well as by pointwise calculations by the following equation

$$pK_1^H = pH + \log \frac{\bar{n}_A - 1}{2 - \bar{n}_A} \qquad - 5$$

in the range $1.0 < \bar{n}_A < 2.0$

Metal-ligand stability constants

Very dilute solutions were employed so as to eliminate the possibility of polymerisation. The hydrolysis could also be checked by working at low pH range. The metal-ligand were deviated considerably from the reagent curve from 2.6 pH. From these curves, the metal ligand formation number or the average number of ligands attached per metal ion $\bar{n}$, have been calculated by the formula.

$$\bar{n} = \frac{(V_3 - V_2(N^0 + B^0)}{(V^0 + V_2)\bar{n}_A \cdot T_M} \qquad - 6$$

where T_M = the initial concentration of the metal ion. The $\bar{n}$ values were found to be continuous from B = 2.6 to B = 6.4.

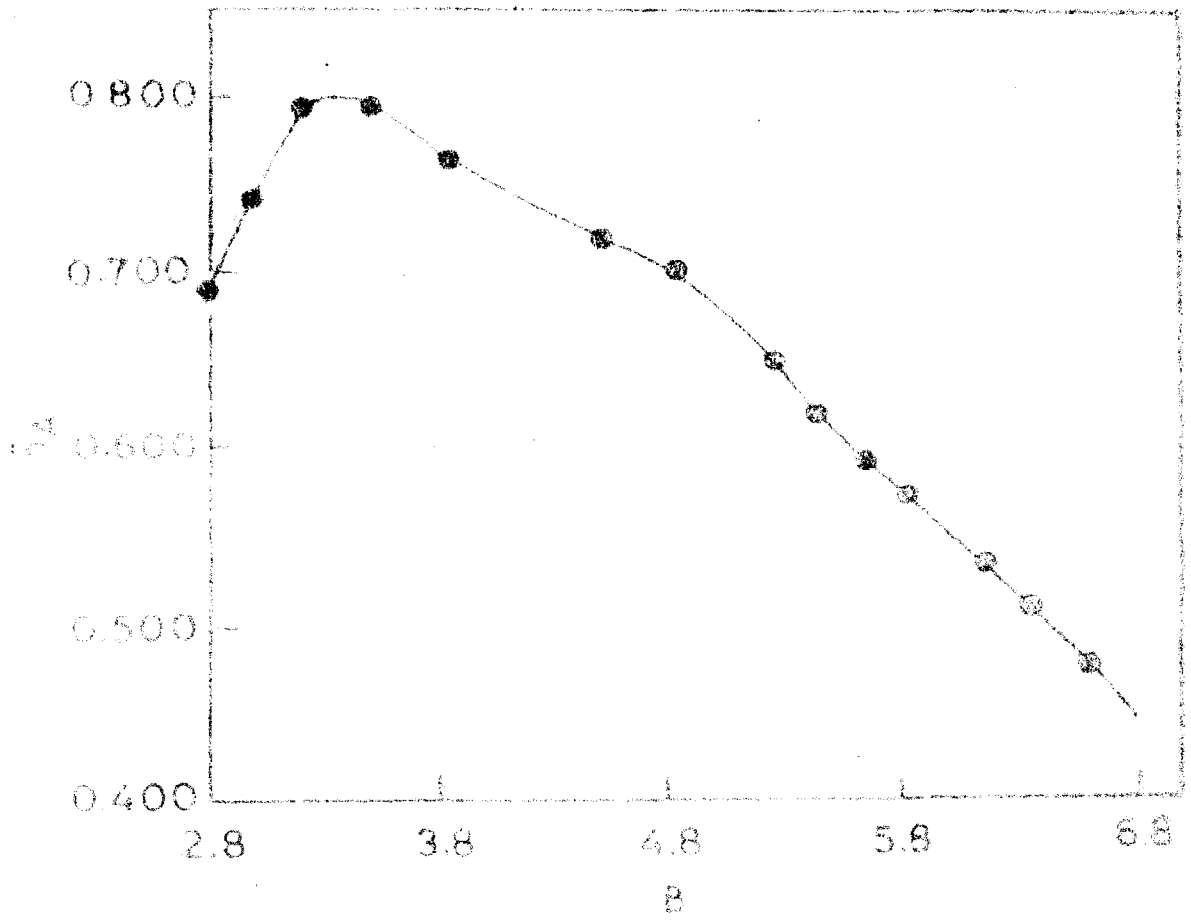


FIG XXXII. TYPICAL PROTON - LIGAND FORMATION CURVE

TABLE - XII

Proton-Ligand Formation Number of AMTDA at 25° and 35°C

pH-meter reading (B)	$\bar{n}_A$ at 25°C		$\bar{n}_A$ at 35°C
	μ=0.05M	μ=0.1M	μ=0.1M
2.6	0.934		0.940
2.7	0.900	0.664	0.928
2.8	0.834	0.732	0.927
3.2	0.868	0.801	0.915
3.4	0.845	0.798	0.903
3.6	0.836	0.768	0.889
3.8	0.800	0.735	0.876
4.2	0.770	0.709	0.852
4.4	0.738	0.669	0.838
4.6		0.645	0.825
5.0	0.718	0.641	0.742
5.2	0.705	0.636	0.709
5.6	0.670	0.636	0.625
6.0	0.635	0.604	0.555
6.2	0.600	0.600	0.515
6.4	0.574	0.539	0.490
6.6	0.540	0.505	0.451
6.8	0.505	0.406	0.384
7.0	0.444	0.307	0.299

The maximum $\bar{n}$ values in all the cases were less than 3.5 showing thereby that only 1:1, 1:2 and 1:3 complexes were formed.

The free ligand exponent (pL) values were calculated at various $\bar{n}$ values using the following equation.

$$pL = \log_{10}\left\{\frac{\text{antilog } B_n \times \frac{1}{\text{antilog } pH} \times (V^0+V_3)}{(T_L - \bar{n}.T_M) \times V^0}\right\} \quad - 7$$

where B_n is the overall proton-ligand stability constant. Approximate values of log K_1, log K_2 and log K_3 were directly read from the metal-ligand formation curves obtained by plotting $\bar{n}$ against pL [Table XX , Fig.XXXIII]

RESULTS AND DISCUSSION

The ligand 2-amino-5-mercapto-1,3,4-thiadiazole is amphoteric in character. The potentialities of forming complexes with the metal ions have been shown by accepting a proton at the amino group and losing a proton at the mercapto group. The values of $\bar{n}_A$ were calculated at B=2.7 and 6.8 and were found to be 0.838 and 0.274 respectively at 25°C whereas at 35°C the values were 0.928 and 0.384 respectively. These values indicated the dissociation of only one proton. Proton ligand stability constant log K_1^H

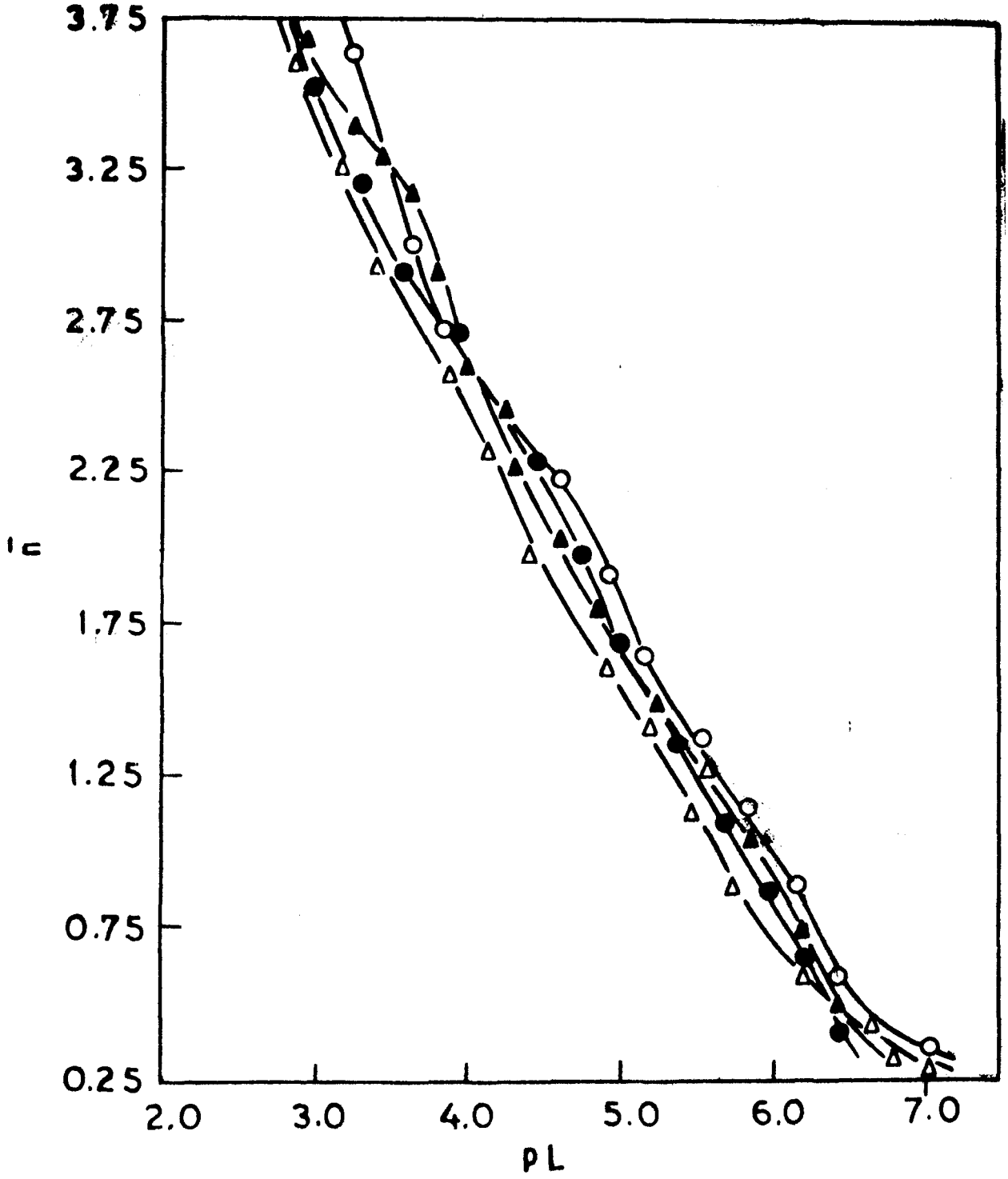


FIG. XXXIII METAL-LIGAND FORMATION CURVE AT 25°C

TABLE - XIII

Proton-Ligand Stability Constant of AMTDA at 25° and 35°C

Stability constant	μ=0.05M at 25°	μ=0.1M at 25°	μ=0.1M at 35°
log K_1^H	6.825 ±0.22	6.625 ±0.27	6.55 ±0.24

TABLE - XIV

Nd(III) Complexes of AMTDA at 25° and 35°C at μ= 0.1M

pH-meter reading (a)	25°C		35°C	
	$\bar{n}$	pL	$\bar{n}$	pL
2.6			0.454	6.378
2.8	0.501	6.416	0.567	6.193
3.2	0.827	6.052	0.723	5.812
3.4	0.827	5.882	0.844	5.769
3.6	0.859	5.657		
4.0	1.343	5.312	1.006	5.043
4.2	1.638	5.149	1.100	4.855
4.6	1.872	4.781	1.297	4.477
5.0	2.323	4.441	1.507	4.104
5.2	2.489	4.277	1.618	3.918
5.6	2.619	3.901	1.954	3.564
6.0	2.878	3.451	2.382	3.230
6.2	2.980	3.375	2.803	3.107
6.4	3.158	3.228	3.305	3.020

TABLE - XV

Sm(III) Complexes of AMTDA at 25° and 35°C at μ = 0.1M

pH-meter reading	25°C		35°C	
	$\bar{n}$	pL	$\bar{n}$	pL
2.6			0.455	6.378
2.8	0.455	6.411	0.528	6.189
3.2	0.794	6.048	0.604	5.798
3.4	0.825	5.858	0.682	5.608
3.6	1.076	5.680	0.764	5.416
4.0	1.343	5.312	0.935	5.041
4.2	1.474	5.128	1.024	4.845
4.6	2.066	4.809	1.211	4.466
5.0	2.451	4.471	1.518	4.105
5.2	2.581	4.293	1.677	3.925
5.6	2.721	3.996	2.105	3.586
6.0	2.990	3.574	2.601	3.269
6.2	3.107	3.418	2.919	3.131
6.4	3.257	3.231	3.203	2.995

TABLE - XVI

Cd(III) Complexes of AMTDA at 25° and 35°C at μ = 0.1M

pH-meter reading	25°C		35°C	
	$\bar{n}$	pL	$\bar{n}$	pL
2.6			0.352	6.370
2.7	0.503	6.515		
2.8	0.710	6.339	0.940	6.231
3.2	0.829	6.052	1.004	5.842
3.4	1.237	5.898	0.964	5.639
3.6	1.288	5.705	1.192	5.464
4.0	1.640	5.349	1.339	5.083
4.2	1.813	5.172	1.396	4.689
4.6	2.242	4.836	1.648	4.521
5.0	2.451	4.470	1.897	4.157
5.2	2.489	4.275	2.039	3.976
5.6	2.619	3.900	2.134	3.590
6.0	2.991	3.575	2.636	3.275
6.2	3.107	3.419	3.037	3.176
6.4	3.306	3.331	3.413	3.048

TABLE - XVII

Tb(III) Complexes of AMTDA at 25° and 35°C at μ= 0.1M

pH-meter reading	25°C		35°C	
	$\bar{n}$	pL	$\bar{n}$	pL
2.6			0.422	6.375
2.7	0.000	6.468		
2.8	0.441	6.410	0.451	6.181
3.2	0.773	6.046	0.618	5.801
3.4	1.202	5.809	0.645	5.604
3.6	1.249	5.701	0.894	5.431
4.0	1.361	5.314	0.902	5.032
4.2	1.813	5.192	0.985	4.841
4.6	2.239	4.836	1.180	4.463
5.0	2.239	4.436	1.438	4.094
5.2	2.489	4.277	1.664	3.923
5.6	2.618	3.900	2.226	3.604
6.0	2.878	3.451	2.927	3.332
6.2	2.982	3.373	3.041	3.156
6.4	3.137	3.208	3.414	3.049

TABLE - XVIII

Dy(III) Complexes of ANTDA at 25° and 35°C at μ= 0.1M

pH-meter reading (B)	25°C		35°C	
	$\bar{n}$	pL	$\bar{n}$	pL
2.6			0.170	6.351
2.8	0.500	6.467	0.525	6.188
3.2	0.794	6.049	0.732	5.812
3.4	0.825	5.853	0.817	5.622
3.6	1.029	5.614	0.927	5.434
4.0	1.345	5.314	1.093	5.053
4.2	1.638	5.072	1.377	4.886
4.6	1.871	4.781	1.456	4.496
5.0	1.924	4.389	1.919	4.158
5.2	2.489	4.275	2.082	3.982
5.6	2.618	3.900	2.314	3.618
6.0	2.990	3.575	2.646	3.276
6.2	3.107	3.418	2.984	3.144
6.4	3.257	3.231	3.504	3.073

TABLE - XIX

Ho(III) Complexes of AHDTDA at 25° and 35°C at μ= 0.1M

pH-meter reading (B)	25°C		35°C	
	$\bar{n}$	pL	$\bar{n}$	pL
2.6			0.352	6.368
2.7	0.000	6.474		
2.8	0.455	6.412	0.543	6.189
3.2	0.794	6.048	0.558	5.795
3.4	1.257	5.878	0.743	5.614
3.6	1.288	5.705	0.758	5.417
4.0	1.406	5.319	0.961	5.039
4.2	1.873	5.181	1.079	4.852
4.6	2.324	4.849	1.318	4.479
5.0	2.323	4.449	1.578	4.112
5.2	2.581	4.293	1.781	3.939
5.6	2.721	3.996	2.358	3.626
6.0	2.991	3.574	3.032	3.354
6.2	3.092	3.399	3.551	3.287
6.4	3.259	3.238	3.974	3.238

was obtained from the proton-ligand formation curve by half integral method. This value was also compared with the value calculated by pointwise method.

The approximate values of stability constants, Log K_1, Log K_2 and Log K_3 directly read from the curve of $\bar{n}$ Vs. pL at $\bar{n}$ = 0.5, 1.5 and 2.5 respectively were compared with the values obtained from the pointwise calculation using the equations.

$$\log K_1 = pL - \log \frac{(1-\bar{n})}{\bar{n}} \qquad - 8$$

$$\log K_2 = pL - \log \frac{2-\bar{n}}{\bar{n}-1} \qquad - 9$$

The values of the standard deviations were calculated for the proton-ligand stability constant and the metal ligand stability constant with the help of the equation,

$$\sigma = \left[\frac{(\bar{n}_{expt.} - \bar{n}_{cal.})^2}{N} \right]^{1/2} \qquad - 10$$

where N is the number of observation.

The overall changes in free energy (ΔG_n), enthalpy (ΔH_n) and entropy (ΔS_n) have been calculated using the equations and the values are computed (Table XXI, XXII and XXIII).

TABLE - XX

Stability Constants of Rare Earth Complexes with AMTDA at 25° and 35°C

Metal	Log K_1		Log K_2		Log K_3		Log K_n	
	25°	35°	25°	35°	25°	35°	25°	35°
Nd	6.416±0.29	6.176±0.31	5.200±0.22	5.000±0.27	4.200	4.040	15.816	15.216
Sm	6.375±0.25	6.176±0.15	5.200±0.26	5.010±0.24	4.175	4.005	15.750	15.191
Gd	6.500±0.27	6.240±0.25	5.400±0.08	5.180±0.25	4.275	4.095	16.175	15.515
Tb	6.375±0.26	6.120±0.06	5.250±0.13	5.035±0.27	4.200	4.025	15.825	15.280
Dy	6.475±0.17	6.220±0.02	5.225±0.25	5.015±0.26	3.900	3.735	15.600	14.970
Ho	6.425±0.24	6.240±0.20	5.275±0.02	5.095±0.26	4.055	3.905	15.755	15.240

TABLE - XXI

Free Energy of the Formation of Rare Earth Complexes with AMTDA at 25° and 35°C

Metal	$-\Delta G_1$ Kcal.mole^{-1}		$-\Delta G_2$ Kcal.mole^{-1}		$-\Delta G_3$ Kcal.mole^{-1}		$-\Delta G_n$ Kcal.mole^{-1}	
	25°	35°	25°	35°	25°	35°	25°	35°
Nd	8.718	8.674	7.066	7.023	5.707	5.674	21.500	21.371
Sm	8.660	8.674	7.066	7.008	5.671	5.624	21.400	21.306
Gd	8.831	8.760	7.336	7.275	5.808	5.750	21.980	21.785
Tb	8.660	8.592	7.134	7.074	5.707	5.652	21.510	21.318
Dy	8.796	8.732	7.099	7.042	5.299	5.246	21.190	21.020
Ho	8.728	8.760	7.166	7.155	5.509	5.485	21.420	21.400

TABLE - XXII

Enthalpy of Reaction of Rare Earth Metals with AMTDA at 25° and 35°C

Metal	ΔH_1 (Kcal.mole^{-1})		ΔH_2 (Kcal.mole^{-1})		ΔH_3 (Kcal.mole^{-1})		ΔH_n (Kcal.mole^{-1})	
	25°	35°	25°	35°	25°	35°	25°	35°
Nd	9.720	10.382	8.097	8.652	6.477	6.921	24.284	25.952
Sm	8.059	8.608	7.693	8.221	6.832	7.353	22.634	24.182
Gd	10.530	11.247	8.904	9.517	7.283	7.787	26.717	28.541
Tb	10.327	11.031	8.714	9.301	7.084	7.570	26.125	27.902
Dy	10.327	11.031	8.502	9.084	6.680	7.139	25.509	27.254
Ho	7.493	8.003	7.288	7.787	5.683	5.930	20.464	21.780

TABLE - XXIII

Entropy of Reaction of Rare Earth Metals with AMTDA at 25° and 35°C

Metal	ΔS_1 (Cal.deg^{-1}.mole^{-1})		ΔS_2 (Cal.deg^{-1}.mole^{-1})		ΔS_3 (Cal.deg^{-1}.mole^{-1})		ΔS_n (Cal.deg^{-1}mole	
	25°	35°	25°	35°	25°	35°	25°	35°
Nd	61.8	61.5	50.9	50.9	40.88	40.89	153.58	153.29
Sm	56.1	56.1	49.5	49.4	42.12	42.13	147.72	147.63
Gd	65.0	65.0	54.49	54.52	43.93	44.00	163.42	163.52
Tb	64.0	63.7	53.18	53.16	42.92	42.92	160.10	159.78
Dy	63.7	64.2	52.35	52.36	40.26	40.21	156.21	156.77
Ho	54.4	54.4	48.5	48.51	37.22	37.26	140.12	140.17

1. $\Delta G = - RT \ln K,$ - 11

2. $\frac{d \log K}{d(\frac{1}{T})} = \frac{\Delta H}{4.57}$ and - 12

3. $T. \Delta S = \Delta H - \Delta G$ - 13

ΔG values are almost similar whereas ΔH and ΔS values differ considerably. The positive values of enthalpy change and increase in entropy[160,161] have been attributed to the presence of metal chelate bond causing greater sterric strain. The formation of 1:2 and 1:3 complexes appear to be less endothermic and the values of ΔH and ΔS are less positive than those of the 1:1 complex. This is completely in agreement[162] with the expectation of less dehydration of the cation and probable degree of covalency in the metal-ligand bonding. The greater the sterric hinderance of the complex, the greater will be the values of log K_1/K_2. The deviation in the stability order is also caused by the π-bonding tendency[163] of the sulphur atom with the metal ion.

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